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# Report on the Feasibility of APEG Detcxification of Dioxin-Contaminated Soils

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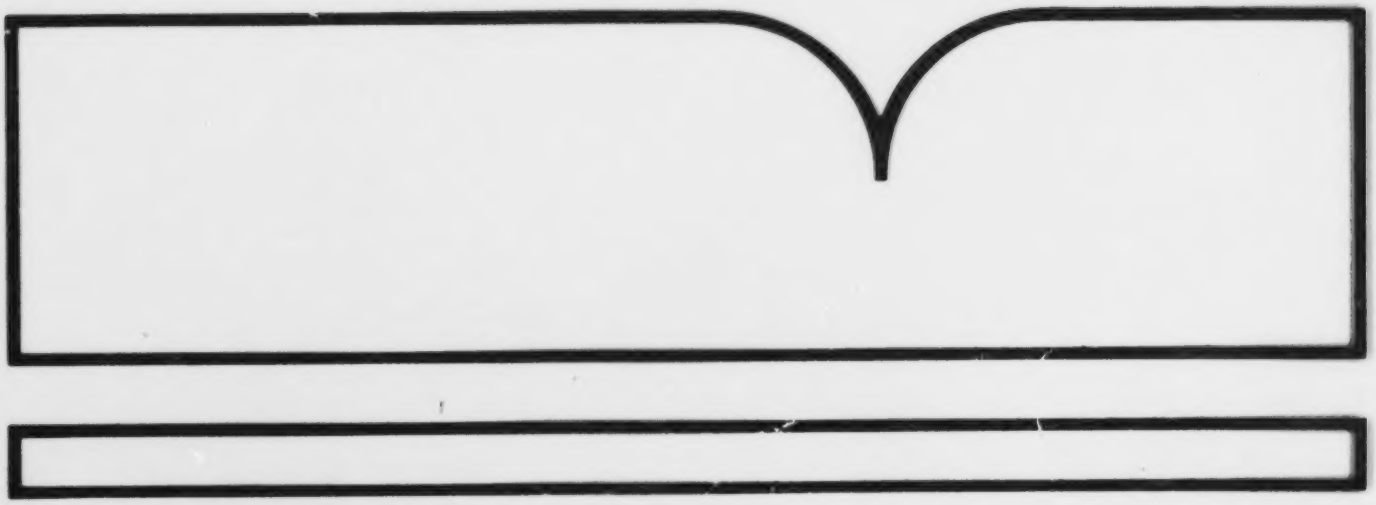

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# REPORT ON THE FEASIBILITY OF APEG DETOXIFICATION OF DIOXIN-CONTAMINATED SOILS

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by

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All chemical analyses were performed by Dr. T. O. Tiernan and staff, Wright State University, Dayton, OH.

16. ABSTRACT

The project was designed to verify in proof-of-principle studies, the efficacy of newly developed chemical reagents to destroy 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) dissolved in a solvent (toluene) and in contaminated soil samples from two locations in Missouri.

The study demonstrated that alkali based polyethylene glycol reagents under ambient conditions can completely destroy within 48 hours 510 nanograms of TCDD dissolved in toluene. Also, in laboratory studies the APEG reagents significantly reduced within 21 days the 330 ppb of TCDD in a Missouri soil by 25 percent with a single APEG application and 68 percent with two APEG applications.

This study has accomplished its proof-of-principle objective, however, further research is required and is to be initiated in FY-84 to establish optimal methods for applying APEGs to TCDD, PCBs and other toxic haloorganics in contaminated soils and waste materials.

17. KEY WORDS AND DOCUMENT ANALYSIS

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## EXECUTIVE SUMMARY

This report describes proof-of-principle studies conducted by the U. S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Cincinnati, Ohio, in conjunction with the Wright State University, Dayton, Ohio, to determine the ability of newly-developed chemical reagents to destroy 2,3,7,8-tetrachlorodibenzo-p-dioxin (referred to in this report simply as "TCDD") in contaminated soil samples from two locations in Missouri. These novel reagents are based upon the reaction of alkali metals or their hydroxides with polyethylene glycols or their derivatives. For convenience, we refer to these reagents generically as "APEGs". The following code is used for specific reagents:

(1) K for potassium;
(2) M for monomethyl polyethylene glycol ether (absence indicates that the ordinary form of polyethylene glycol was used);
(3) A number indicating the average molecular weight of the glycol.

For example, KM-350 indicates a reagent made from reacting potassium (metal or hydroxide) with a monomethyl polyethylene glycol ether of average molecular weight 350, and K-120 indicates a reagent made from reacting potassium (metal or hydroxide) with a polyethylene glycol of average molecular weight 120.

### Phase I

Two APEGs were involved in the first phase of these studies: (1) K-400 and (2) K-120. These reagents were used both with "neat" solutions of 510 nanograms TCDD (i.e., solutions containing TCDD dissolved in toluene; no soils were present) and with two types of Missouri soils: (1) Denny Farm and (2) Timberline Stables. The organic chlorine contents of these two soils were, respectively, 1380 ppm and 15.3 ppm; their TCDD contents were, respectively, 330 (± 33 ppb) and 277 (± 28 ppb). The results of these tests were as follows:

(1) With regard to the neat solutions, the K-120 destroyed virtually all of the TCDD within a 2-day period. The results with K-400, however, were indeterminate because the reagent was not miscible with the toluene solution of TCDD.*

(2) The percent reduction in TCDD from the original levels in the soil samples was as follows:

---

* The K-400 reagent used in Phase I was prepared using a 66% aqueous KOH solution and therefore was not miscible with toluene.

TABLE EX-1

Percent Reduction from Initial TCDD Levels

| | Timberline | | Denny | |
|---|---|---|---|---|
| | K-400 | K-120 | K-400 | K-120 |
| 7 days | 45% | 46% | nm | 51% |
| 28 days | 35% | 38% | 12% | 5% |

nm = not measured

The TCDD reduction data varied cyclically throughout the 4 weeks of the tests, with the samples showing an anomalous final TCDD reduction, at 28 days, lower than that observed after 7 days. Furthermore, the variability of replicate analyses was quite high; in some cases the variability, expressed as a coefficient of variation, was as high as 40%.

Phase II

It was decided to conduct a series of supplementary experiments, which involved alterations in sample preparation and in analytical procedure, to try to discover the source of this high variability and perhaps an explanation for the anomalous 7- versus 28-day results. The experiments conducted, and the results, are summarized as follows:

(1) There was no statistical evidence that exhaustive Soxhlet extraction, even with fresh solvent and with extraction times of up to 32 hours, extracted more TCDD than bottle extraction with extraction times of no more than 3 hours.

(2) Although statistically significant differences do exist between "unconditioned" and "conditioned" soils (by "conditioning" is meant the addition of HCl, potassium hydroxide or polyethylene glycol to the soil sample, followed by analysis for TCDD), the size of these differences is relatively unimportant. The following averages illustrate the differences found (the glycol used had an average molecular weight of 400 and is referred to as "PEG-400" in the listing below):

| | |
|---|---|
| Unconditioned: | 292 ppb |
| With HCl: | 302 ppb |
| With KOH: | 313 ppb |
| With PEG-400: | 317 ppb |

Thus neither the individual components of the reagent itself nor the quench chemical used in the analytical procedure (i.e., the HCl) appreciably affects the amount of TCDD released from a soil sample during analysis. Furthermore, this observation is valid regardless of the period of time, up to 8 hours, that the chemicals are in contact with the soil.

(3) There is no measurable time effect, up to 8 hours, on the recovery of the internal standard (37-Cl-labeled dioxin) after addition to the sample. Thus the amount of time (up to 8 hours) that samples stand after adding the internal standard does not affect the precision of the results.

(4) During these supplementary experiments, the precision of the analyses increased dramatically over that observed in the first series. Since the soil samples in the supplementary series were considerably more homogeneous than in the first (in the supplementary series the samples were sieved, intermixed and ground in a ceramic ball mill containing Borundum grinding media; in the first series the samples were sieved and intermixed only), it was concluded that inadequate sample preparation was the main cause of the anomalous results shown in Table EX-1. It is now clear that the TCDD is not present uniformly distributed throughout the soil samples and therefore it is imperative that soil samples be thoroughly homogenized before subjecting them to treatment with APEG reagents in laboratory studies.

Phase III

As a consequence of these supplementary studies, a third (and last) series of experiments was conducted that essentially was designed as a repetition of phase one. However, during the interim between phase one and phase three of this study, new APEG reagents were tested that appeared to be much more reactive than K-120. Thus, K-120 was replaced by one of these new reagents, i.e., KM-350, in this last phase. In addition, the K-400 reagent used in Phase III was prepared directly from KOH pellets, rather than the 66% aqueous KOH solution used in Phase I. Only Denny Farm soil was used in the phase III experiments. The results were as follows (in percent reduction in TCDD from the original level in the Denny Farm soil):

TABLE EX-2

Percent Reduction from Initial TCDD Levels

| | Denny Farm Soil | |
|---|---|---|
| | K-400 | KM-350 |
| 1 day | 8% | 15% |
| 7 days | 19% | 27% |
| 14 days | 16% | 36% |
| 21 days | 25% | 42% |
| 28 days | 22% | 43% |

The anomalies in the apparent decrease of the TCDD level of K-400 treated sample at day 14 was found not to be statistically significant.

To test the effect of a multiple application of an APEG reagent, a sample of Denny Farm soil was treated with K-400 and, 12 days later, a second application was made. Table EX-3 summarizes the percent reduction in TCDD observed, along with a repetition of days 14 and 21 in the single application data of Table EX-2 for comparison:

TABLE EX-3

Percent Reduction in Starting TCDD Levels

| | Denny Farm Soil Treated with K-400 | |
|---|---|---|
| | Single Application | Repeat Application |
| 14 days | 16% | 56% |
| 21 days | 25% | 68% |

The results of this study clearly indicate that APEG reagents can, under certain laboratory conditions, significantly reduce the levels of TCDD in contaminated soils. Future work must, however, concern itself with the following questions:

- What is the toxicological significance of by-products of APEG-dioxin reactions in soils?
- Can additives be found (surfactants, wetting agents, etc.) to increase and accelerate the contact between the reagent and TCDD that is tightly-bound to soil particles and other materials commonly found in soils?
- Are there other processes (radio frequency heating, photolysis, etc.) that can enhance the use of APEG reagents on contaminated soils?
- What are the optimal methods for applying APEGs to soils and maintaining the integrity of the site (prevention of water influx, etc.) during the reaction period?

INTRODUCTION

Unplanned and uncontrolled deposition of hazardous wastes on the ground may severely damage terrestrial ecosystems and destroy or diminish opportunities for land use. The presence of large quantities of contaminated soils which remain on site following emergency cleanup may also endanger water resources through runoff and erosion and/or leaching into groundwater. The accumulation of polychlorinated biphenyls (PCBs) and chlorinated dibenzodioxins (CDDS) in soils, sediments and living tissue, for example, is a serious problem that has received considerable public attention in recent years. Hazardous chemicals have contaminated areas large enough, however, so that in situ treatment may be the only practical or economically acceptable approach to treatment, health and environmental protection, land reclamation and ultimate disposal.

In the chemistry laboratory at the Franklin Research Center (FRC) during the summer of 1978 a new family of chemical reagents was synthesized. These novel reagents are based upon reaction of alkali metals or their hydroxides with polyethylene glycols or their derivatives. For convenience, we refer to these reagents generically as "APEGs". APEGs dehalogenate haloorganic compounds of many types--in open air (aerobic) systems at ambient (room) temperatures. In August of 1979 the U.S. Environmental Protection Agency (USEPA) provided grant support to FRC to investigate the chemistry underlying the dehalogenation process, concentrating on dechlorination of PCBs in mineral oils. Subsequent EPA grant assistance was provided for a limited study of the effects of an APEG reagent on PCB-contaminated soil. This research is in progress. Additional APEG research has since been conducted by the General Electric Company, the Galson Research Corporation, the USEPA Industrial Environmental Research Laboratory in Cincinnati (IERL-Ci), the University of Cincinnati and other Universities.

Late in 1982 it came to the attention of the USEPA Assistant Administrator for Solid Waste and Emergency Response that APEG reagents might be effective against chlorinated dioxins. Since chlorinated dioxins represent a critical health hazard in a number of areas, especially in Missouri, the IERL-Ci was directed to begin an immediate program to determine, at the proof-of-principle level, the potential effectiveness of these reagents for in situ destruction of chlorinated dioxins in contaminated soils. As Wright State University (WSU), which is widely recognized as being highly expert in dioxin analysis, was already conducting such analyses of various Missouri soils, IERL-Ci developed a joint program that involved WSU in an analytical role. A draft protocol for the planned tests was submitted by WSU in Novmeber 1982. The final protocol, "Determination of the Efficacy of Selected Chemical Reagents to Destroy 2,3,7,8-TCDD and Other Haloorganics in Contaminated Soils", prepared by C. Rogers of IERL-Ci in collaboration with WSU, was approved in December 1982. The ultimate objective of the program outlined in this protocol document is the development of a reliable and cost-effective technique for the destruction and/or detoxification of toxic halogenated organic wastes, particularly highly

toxic compounds such as 2,3,7,8-TCDD present in contaminated soils at dumpsites and in road beds and horse arenas which have been coated with dioxin-containing waste oils in Missouri and elsewhere. The specific objective of the project, which is the subject of this report, was to determine, at the proof-of-principle level, whether selected APEG reagents at ambient temperatures have practical potential for the destruction of 2,3,7,8-TCDD and other hazardous chlorinated organics in soils.

## II. EXPERIMENTAL PROCEDURES

The experiments basically involved, a) the preparation of soil samples and solutions; b) treatment of samples with two different APEG reagents, and c) at predetermined time intervals of 7, 14, 21 and 28 days following the treatment the reagent in the samples was destroyed or "quenched" (with HCl) and the samples analyzed for 2,3,7,8-TCDD content. In addition to the treated samples, untreated control samples were also analyzed for TCDD. Several additional types of analyses were also accomplished, as described below, in order to provide information useful in determining optimal treatment procedures.

### A. Reagents

The following code is used for specific reagents:

(1) K for potassium;
(2) M for monomethyl polyethylene glycol ether (absence indicated that the ordinary form of polyethylene glycol was used);
(3) A number indicating the average molecular weight of the glycol.

For example, KM-350 indicates a reagent made from reacting potassium (metal or hydroxide) with a monomethyl polyethylene glycol ether of average molecular weight 350, and K-120 indicates a reagent made from reacting potassium (metal or hydroxide) with a polyethylene glycol of average molecular weight 120.

Two reagents selected for application in the TCDD contaminated soils, i.e., K-120 and K-400. The K-120 reagent was prepared by reacting at 90°C stoichiometric proportions of potassium metal with polyethylene glycol molecular weight 120. The K-400 reagent was prepared by mixing stoichiometric proportions of polyethylene glycol molecular weight 400 with a 66% aqueous KOH solution.

### B. Preparation of TCDD Solutions and Contaminated Soil Samples for Treatment with KPEG Reagents

On November 9, 1982, bulk batches of two TCDD-contaminated soils, one from the Timberline Stables site and one from the Denny Farm site, both located in Missouri, were transported directly to Wright State University by personnel of the USEPA Region VII, Kansas City, Kansas.

The soil samples received actually consisted of six 1-gallon cans of each of the two soils (a total of 12 cans), and it had been previously agreed that Wright State University would attempt to produce one large homogeneous composite sample of each of the two soils (Timberline Stables and Denny Farm) for use in the dehalogenation tests. Upon receipt, the soil samples in the

several 1-gallon cans were visually observed to be of markedly different composition. The appearance of these was as follows:

Samples Constituting WSU Sample No. EHK-1 (EPA No. AY6501)
Timberline Stables

| Can No. | Appearance of Contents |
|---|---|
| 1 | Sandy soil, moderately dry |
| 2 | Clay, moderately wet |
| 3 | Surface soil, dust and loose dirt |
| 4 | Mixture of various soil types, moderately wet |
| 5 | Sandy soil/Clay (2/1 mixture) |
| 6 | Heavy clay, very wet (saturated) |

Samples Constituting WSU Sample No. EHK-2 (EPA No. AY6502)
Denny Farm Site

| Can No. | Appearance of Contents |
|---|---|
| 1 | Mostly large gravel, small amount of soil |
| 2 | Mostly large gravel, small amount of soil |
| 3 | Gravel/fine soil or sand mixture |
| 4 | Gravel/fine soil or sand mixture |
| 5 | Large and small gravel and sand |
| 6 | Gravel/fine soil or sand mixture |

The contents of Can 6 of Sample EHK-1 and of Cans 1 and 2 of Sample EHK-2 were not included in the composite samples prepared because these were too wet in the first instance, and mostly gravel in the second case (note that stones were to be removed from the composite samples by subsequent screening). Accordingly, composite samples were prepared by blending portions of Cans 1, 2, 3, 4, and 5 for Sample EHK-1 and portions of Cans 3, 4, 5, and 6 for Sample EHK-2. The procedures utilized are as follows. Working entirely with an enclosed glovebox into which the samples were placed, approximately equal portions of each of the samples constituting each composite were removed and placed in a container of about 8-liter size. The mixture was then passed through a No. 5 Mesh size (4mm) sieve. Larger aggregates and pieces of soil which would not initially pass through the sieve were ground with a mortar and pestle until the particle size was small enough to pass through the screen. Stones and larger debris retained in the sieve were discarded. After the two composite samples had been sieved and collected in a single container, portions of each sample were poured back and forth between the large container and two clean cans about 15 times to create two reasonably homogeneous samples for use in the tests. Finally, two clean 1-gallon cans of each of the composite samples were filled (not quite full) and then were sealed and stored to await use in the tests. Each of these cans was rolled vigorously to thoroughly agitate and mix the contents, i.e., as a final attempt at homogenization. Aliquots of each of the composite samples were removed for determination of water and total organic chlorine content, and an initial estimation of the TCDD content.

On Dec. 13, 1982, shortly prior to the time of treatment of the samples, aliquots of each of the composite samples were removed from the containers, weighed and transferred to separate 125 mL beakers which were tightly covered with aluminum foil. Some 130 test beakers of soil were prepared in this manner and placed in two self-contained hoods (designed for handling toxic materials) which fully filter both the intake and exhaust air through HEPA and charcoal filters. Each of the beakers was labeled with an identifying sample code number, corresponding to its use for a particular time-phased test experiment. The plan of these experiments and the corresponding sample numbers are shown in Table 1. Also prepared at the same time, and placed in other 125 mL beakers, were toluene and acetone solutions containing 2,3,7,8-TCDD, and associated solvent and reagent blank samples, (listed in Table 2) some of which were subsequently treated with APEG reagents along with the soil samples.

## III. TREATMENT OF SOIL SAMPLES AND TCDD SOLUTIONS WITH APEG REAGENTS

On December 15, 1982, Charles Rogers of USEPA/IERL-Ci, and Frank Iaconianni of Franklin Research Center, Philadelphia, PA, arrived at Wright State University, Dayton, OH, with the two APEG reagents (K-400 and K-120, respectively) previously mentioned. The EPA and FRC scientists then proceeded, with assistance from WSU scientists, to apply the reagents to the various test beakers which had been prepared as described above. The quantities of reagent applied were determined prior to the tests on the basis of data on the total organic chlorine content of the two samples (Timberline Stables and Denny Farm) provided to EPA/IERL-Ci by WSU. Previous laboratory studies, for example, demonstrated that an APEG:Chlorine molar ratio of 10:1 was effective in the dehalogenation of haloorganic compounds. However, upon applying reagent to soils, it was determined that the quantity of reagent was insufficient to completely wet the soils to provide intimate pollutant-reagent contact. It was necessary to apply approximately 21-30 mL of K-120 to each sample treated with this reagent, and approximately 14-30 mL of K-400 to samples treated with that reagent. The molar ratios of APEG reagents to organochlorine (APEG:Cl) in the thoroughly-wetted soils were as follows: Timberline 860:1 and Denny Farm 180:1. After addition of the reagents, the contents were thoroughly mixed by stirring and the sample beakers were again tightly covered with aluminum foil and returned to the hoods. The samples were weighed following completion of all applications, and the weights of reagents added in each case are shown in Appendix I. As already mentioned, treated and control samples are identified by number in Table 1.

## IV. ANALYSES OF CONTROLS AND APEG-TREATED SAMPLES

Following treatment of the samples, 5 grams of each of the treated and control samples were removed from the test vessels and analyzed for 2,3,7,8-TCDD content at predetermined intervals according to the schedule indicated in Table 1. Several other types of analyses were also accomplished, as will be described below.

### A. Water Content

Aliquots of each of the two composite samples were removed, weighed, and dried in a vessel placed in a sand bath heated at 55°C, while purified $N_2$ was passed over the sample. The weight of the sample was determined periodically

TABLE 1

SAMPLE VESSEL NUMBERS FOR

TCDD DESTRUCTION TESTS ON CONTAMINATED SOILS

| Number of days following treatment when reaction terminated | Untreated controls | Untreated controls with spiked $^{37}Cl_4$-TCDD | Treated with K-400 | Treated with K-120 |
|---|---|---|---|---|
| 24 hrs. | FDE-23 | FDE-92 | FDE-25 | FDE-1 |
| | FDE-24 | FDE-125 | FDE-26 | FDE-3 |
| | FDE-43 | | FDE-27 | FDE-45 |
| | FDE-69 | | | FDE-51 |
| | FDE-70 | | | FDE-52 |
| | FDE-71 | | | FDE-53 |
| 7 days | FDE-19 | FDE-94 | FDE-28 | FDE-4 |
| | FDE-21 | FDE-127 | FDE-29 | FDE-5 |
| | FDE-22 | | FDE-30 | FDE-6 |
| | FDE-72 | | | FDE-54 |
| | FDE-73 | | | FDE-55 |
| | FDE-74 | | | FDE-56 |
| 14 days | FDE-2 | FDE-126B | FDE-31 | FDE-7 |
| | FDE-20 | FDE-128 | FDE-32 | FDE-8 |
| | FDE-75 | | FDE-33 | FDE-9 |
| | FDE-76 | | FDE-63A | FDE-57 |
| | FDE-77 | | | FDE-58 |
| | FDE-107 | | | FDE-59 |
| 21 days | FDE-48 | FDE-124 | FDE-34 | FDE-10 |
| | FDE-49 | FDE-95 | FDE-35 | FDE-11 |
| | FDE-50 | | FDE-36 | FDE-12 |
| | FDE-78 | | FDE-63B | FDE-60 |
| | FDE-79 | | FDE-64A | FDE-61 |
| | FDE-80 | | FDE-65A | FDE-62 |
| 28 days | FDE-44 | FDE-91 | FDE-37 | FDE-13 |
| | FDE-46 | FDE-93 | FDE-38 | FDE-14 |
| | FDE-47 | | FDE-39 | FDE-15 |
| | FDE-81 | | FDE-63C | FDE-51B |
| | FDE-82 | | FDE-64B | FDE-52B |
| | FDE-83 | | FDE-65B | FDE-53B |
| 35 days | FDE-23B | FDE-90 | FDE-40 | FDE-16 |
| | FDE-24B | FDE-129 | FDE-41 | FDE-17 |
| | FDE-84 | | FDE-42 | FDE-18 |
| | FDE-85 | | FDE-63D | FDE-54B |
| | FDE-86 | | FDE-64D | FDE-55B |
| | FDE-130 | | FDE-65D | FDE-56B |

TABLE 2

TESTS ON TCDD SOLUTIONS AND CORRESPONDING CONTROLS

AND BLANKS

| WSU Sample No. | Solvent | Total 2,3,7,8-TCDD Content | Reagent Added | Time After Preparation When Reaction Terminated |
|---|---|---|---|---|
| FDE-117 | Toluene | 510ng TCDD | K-120 | 48 hrs. |
| FDE-118 | Toluene | 510ng TCDD | K-120 | 96 hrs. |
| FDE-120 | Toluene | 510ng TCDD | K-400 | 48 hrs. |
| FDE-119 | Toluene | 510ng TCDD | K-400 | 96 hrs. |
| FDE-112 | -- | -- | K-400 | -- |
| FDE-115 | -- | -- | K-120 | -- |
| FDE-121 | Toluene | -- | K-400 | -- |
| FDE-116 | Toluene | -- | K-120 | -- |
| FDE-110 | Acetone | 510ng TCDD | K-400 | 48 hrs. |
| FDE-108 | Acetone | -- | K-400 | -- |
| FDE-109 | Acetone | 510ng TCDD | K-120 | 48 hrs. |
| FDE-114 | Toluene | -- | None | -- |
| FDE-131 | Acetone | -- | None | -- |
| FDE-112B | -- | -- | K-400 | 96 hrs. |

until no further loss of water or volatiles occurred. Results of these determinations revealed that the water content of composite soil samples from Timberline Stables and Denny Farm were 11.8 and 4.8%, respectively.

B. Total Organic Chlorine

Total organic chlorine was determined in aliquots from each of the two composite samples using the analytical methodology described in the protocol presented in Appendix III of this report. The organic chlorine content of the Timberline soil was 15.3 ppm and, for the Denny Farm soil, 1380 ppm.

C. 2,3,7,8-TCDD Content

Aliquots of the treated and control samples were analyzed for 2,3,7,8-TCDD utilizing the procedures described in the protocol presented in Appendix II of this report. These procedures are consistent with those currently being used in analyses of other Missouri soil samples for EPA/Viar. These EPA approved procedures entail addition of a known quantity of isotopically-labelled 2,3,7,8-TCDD to each sample prior to analysis and which is used as an internal reference standard for quantitation of native TCDD in the sample. The extent of recovery of the added internal standard also provides an indicator of the overall efficacy of the analytical methodology. Since the APEG reagent present in the sample would presumably destroy the added internal TCDD standard (if the reagent is effective), thereby invalidating the analyses of treated samples, it is necessary to destroy any residual reagent in the samples prior to analysis (or at the termination of the time period of a given experiment, if analysis is not immediately accomplished at that point). Accordingly, a reagent "quenching" procedure was developed and applied to each treated sample (and some control samples, in order to ensure that this procedure did not cause problems in the TCDD analyses) prior to analyses of the samples. This procedure is as follows:

1. Add 3.5 mL methanol to the sample.
2. Agitate sample vessel for 10 seconds,
3. Add 8.5 mL 50/50 concentrated HCl/water to the sample.
4. Agitate sample vessel for 10 seconds.
5. Allow the sample to stand for at least 30 minutes (longer periods were more typical) prior to adding the labelled TCDD internal standard and analyzing the sample.

It was observed that the pH of the APEG-treated samples was greater than 10 following application of the APEG reagent, but was lowered to pH = 1, in the case of the K-400 treated samples and to pH = 2 in the case of the K-120 treated samples, following application of the quenching procedure. Therefore, the strongly alkaline APEG reagents were effectively destroyed by this procedure, since the conditions required for their reactivity are no longer met.

## V. PHASE I TEST SERIES RESULTS

All treated samples were "quenched" at the end of the appropriate time interval as indicated by Table 1. Extraction and analyses of the samples for TCDD, which usually require more than one day, were accomplished some time thereafter. Appendix IV presents the dates of quenching, extraction and analyses for all samples through the 28-day period. Appendix IV also lists the measured levels of TCDD as reported by WSU in all samples analyzed, along with relevant analytical and recovery data which are customarily cited.

The mean TCDD concentrations in the various sets of control and APEG-treated samples are summarized in Table 3. Also provided are standard deviations, coefficients of variation, percent recoveries of internal TCDD standard and data on the significance of the difference between the means and the control at the 90% confidence level. Table 3 indicates that there is a cyclical pattern to the apparent TCDD reduction in both types of soils, with an anomalous reduction after 28 days that is lower than the reduction after 7 days. Furthermore, the data indicate high variability in some cases (up to 40%, expressed as a coefficient of variation). Nonetheless, significant (statistically) TCDD reductions of from 45% to 51% were observed after 7 days. After careful review of the variability of the 28-day treatment data, questions were raised regarding the thoroughness of homogenization of soil samples, extraction efficiency of bottle procedures used by WSU, precision of GC-MS analyses, influence of acid or base on release of TCDD from soils, and time dependence of TCDD binding in soils.

## VI. PHASE II (SUPPLEMENTARY VARIABILITY STUDY)

In March 1983 scientists from Wright State University and IERL discusssed and developed a plan for further experiments to examine those factors that were postulated to have influenced the results of Phase I. Each of the sections listed below corresponds to a supplementary study, completed in May 1983, to investigate a specific factor. The detailed protocol is in Appendix V.

### A. Homogenization of Denny Farm Soil

As described in an earlier WSU report (January 26, 1983) on TCDD analysis titled "Tests on the Efficacy of K-400 Reagents for Destruction of 2,3,7,8-TCDD in Contaminated Soil Samples," aliquots of the samples of Denny Farm soil, which had been received previously from EPA, were combined to obtain approximately 2 gallons of soil. The soil was then seived (4mm sieve) and the sieved material was further homogenized by repetitively transferring and intermixing the sieved material. Approximately one gallon of this prepared soil was consumed during Phase I of the degradation studies. The remaining one gallon portion of sieved soil was retained in the original paint can and it is this soil that was further homogenized as described below, in the present studies.

A ceramic ball mill was pre-cleaned using a mixture of Borundum grinding medium and sand and the mill was subsequently washed with methyl alcohol and methylene chloride. The mill was allowed to dry, the soil sample

TABLE 3

STATISTICAL SUMMARY OF WRIGHT STATE DIOXIN DATA

| | Mean[a] | No. of Samples | Std.[a] Dev. | Coeff.of[b] Var., % | Percent[c] Recovery | Sig.[d] @10% ? |
|---|---|---|---|---|---|---|
| A. Timberline Stables | | | | | | |
| 1. Control | 277[e] | 18 | 42.8 | 15 | -- | --- |
| 2. K-400 1-day | 279 | 3 | 37.7 | 14 | 90 | No |
| 3. K-400 7-day | 151 | 3 | 15.5 | 10 | 59 | Yes |
| 4. K-400 14-day | 220 | 3 | 10.3 | 5 | 63 | Yes |
| 5. K-400 21-day | 221 | 3 | 2.3 | 1 | -- | Yes |
| 6. K-400 28-day | 179 | 3 | 14.5 | 8 | -- | Yes |
| 7. K-120 1-day | 230 | 3 | 16.7 | 7 | 91 | Yes |
| 8. K-120 7-day | 149 | 3 | 33.9 | 23 | 32 | Yes |
| 9. K-120 14-day | 201 | 3 | 49.0 | 24 | 64 | Yes |
| 10. K-120 21-day | 224 | 3 | 20.9 | 9 | -- | Yes |
| 11. K-120 28-day | 172 | 3 | 6.2 | 4 | -- | Yes |
| B. Denny Farm | | | | | | |
| 12. Control | 330[e] | 18 | 66.6 | 20 | -- | --- |
| 13. K-120 1-day | 294 | 3 | 32.6 | 11 | 100 | No |
| 14. K-120 7-day | 161 | 3 | 64.6 | 40 | 71 | Yes |
| 15. K-120 14-day | 312 | 3 | 44.9 | 14 | 93 | No |
| 16. K-120 21-day | 276 | 3 | 67.9 | 25 | -- | No |
| 17. K-120 28-day | 315 | 1 | ---- | -- | -- | No |
| 18. K-400 14-day | 298 | 1 | ---- | -- | 86 | --- |
| 19. K-400 21-day | 374 | 3 | 30.7 | 8 | -- | No |
| 20. K-400 28-day | 291 | 2 | 45.3 | 16 | -- | No |
| C. "Replicates"[f] | | | | | | |
| 21. Timberline/Denny | 35[g] | 12 | 34.9 | 15.1[h] | -- | --- |

Note:
a. Mean and Std. Dev. in units of nanograms/gram (ppb);
b. "Coeff. of Var." is the coefficient of variation or the relative standard deviation (i.e., std.dev./mean) expressed as a percentage.
c. "Percent Recovery" refers to the percent recovery of the $^{37}Cl_4$-2,3,7,8-TCDD internal standard.
d. "Sig. @10%" refers to significance of the difference between the mean and the control mean at the 90% confidence level.
e. Tests were made for outliers on the control mean samples, but none could be rejected at the 10% significance level.
f. "Replicate" refers to replicate analyses of same sample extract.
g. Mean in replicate case is average absolute difference.
h. This figure in Line 21 is the average of the individual absolute differences expressed as a percentage of each replicate pair.

TABLE 3 (Continued)

The following are the Wright State University identification numbers of the samples used to calculate the means in the table.

Line 1: FDE-23,24,43,19,21,22,2,20,107,125,127,126B,128,44,48,49,50,129

Line 2: FDE-25,26,27

Line 3: FDE-28,29,30

Line 4: FDE-31,32,33

Line 5: FDE-34,35,36

Line 6: FDE-37,38,39

Line 7: FDE-1,45,3

Line 8: FDE-4,5,6

Line 9: FDE-7,8,9

Line 10: FDE-10,11,12

Line 11: FDE-13,14,15

Line 12: FDE-69,70,71,72,73,74,75,76,77,92,94,78,79,80,90,83,91,93

Line 13: FDE-51,52,53

Line 14: FDE-54,55,56

Line 15: FDE-57,58,59

Line 16: FDE-60,61,62

Line 17: FDE-53B

Line 18: FDE-63A

Line 19: FDE-64A,65A,63B

Line 20: FDE-63C,64B

Line 21: FDE-23,27,29,4,5,70,71,73,74,57

Note: On Line 13, only the first two values (there were three extract replicates made) were included in the calculation.

(the one gallon of Denny Farm soil described above) plus 10 lb. of Borundum grinding media was placed in the mill, and the mill was sealed and rotated for 3 hours. The resulting soil was then removed from the mill and again sieved, this time using a 1mm sieve. This yielded a < 1mm particle size soil fraction, comprising about 40% of the original one gallon of soil. Aliquots of this homogenized soil sample were then utilized in the experiments outlined below.

B. Studies To Assess the Extraction Efficiency Achieved in the Analyses of Homogenized Denny Farm Soil Samples

A series of Soxhlet extractions of aliquots of the homogenized soil prepared as described above were accomplished, and the extracts were analyzed using the GC-MS analytical techniques reported previously. Five aliquots of the homogenized soil (approximately 5 grams each) were placed in precleaned Soxhlet extraction flasks, each of which was charged with 100mL of benzene. Refluxing was begun and continued for various periods. Three of the Soxhlet extractions were conducted for a period of 16 hours and one was extracted for 24 hours, after which times the extracts were removed and analyzed for 2,3,7,8-TCDD (Table 4). The fifth of the five original Soxhlet extracts was conducted for a period of 32 hours, after which the extract (Sample Number 203) was removed and analyzed for 2,3,7,8-TCDD. At this point, two of the three Soxhlet extractors which had been operated for a period of 16 hours were recharged with fresh 100 mL aliquots of benzene, and refluxing was resumed for an additional 16 hours. These extracts (Sample Numbers 204B and 205B) were then removed and analyzed for 2,3,7,8-TCDD. These same two Soxhlet extractors were then recharged with fresh benzene and extraction was resumed for another 16 hour period. These two extracts (Sample Numbers 204C and 205C) were then removed and analyzed for 2,3,7,8-TCDD. Thus, two of the five original soil aliquots were extracted with a total of 300 mL of benzene over a total period of 48 hours.

In addition to the Soxhlet extractions described above, two other aliquots of soil (approximately 5 grams each) were each extracted using the bottle extraction procedure described in the first test series of this project. The two extracts resulting from the bottle extractions (Sample Numbers 227 and 228) were also analyzed for 2,3,7,8-TCDD.

The results of all of the analyses of the samples described above are listed in Table 4.

C. Determinations of the Precision of GC/MS Analyses

Presented in Table 5 are the results of 10 replicate GC-MS analyses (all accomplished on the same day) of a single extract obtained by Soxhlet extraction of a Denny Farm Soil sample. Similarly, in Table 6 are shown the results of 10 replicate GC-MS analyses of the same soil extract obtained by the bottle extraction procedure (again, all analyzed on the same day). In a third set of experiments, aliquots of a single soil extract, obtained by Soxhlet extraction, were withdrawn at various time intervals following extraction and subjected to GC-MS analyses. Results of these analyses are listed in Table 7.

TABLE 4

CONCENTRATIONS OF 2,3,7,8-TETRACHLORODIBENZO-p-DIOXIN DETERMINED TO BE PRESENT IN ALIQUOTS OF HOMOGENIZED DENNY FARM SOIL PREPARED USING VARIOUS EXTRACTION TECHNIQUES

| WSU Sample Number (EHK- ) | Extraction Technique Employed | Concentration of 2,3,7,8-TCDD Found (ng/g) | Percent Recovery of $^{37}Cl_4$-2,3,7,8-TCDD Internal Standard |
|---|---|---|---|
| 201 | Soxhlet (16 hr.) | 292 | 114 |
| 202 | Soxhlet (24 hr.) | 297 | 116 |
| 203 | Soxhlet (32 hr.) | 302 | 108 |
| 204A | Soxhlet (16 hr.) | 294 | 116 |
| 204B | Soxhlet (fresh solvent, 16 hr.) | 0.48 | --- |
| 204C | Soxhlet (fresh solvent, 16 hr.) | 0.20 | --- |
| 205A | Soxhlet (16 hr.) | 290 | 66 |
| 205B | Soxhlet (fresh solvent, 16 hr.) | 0.34 | --- |
| 205C | Soxhlet (fresh solvent, 16 hr.) | 5.0 | --- |
| 206 | 1 hr. HCl, Soxhlet (16 hr.) | 296 | 91 |
| 207 | 24 hr. HCl, Soxhlet (16 hr.) | 303 | 63 |
| 208 | 3 day HCl, Soxhlet (16 hr.) | 314 | 91 |
| 209 | 7 day HCl, Soxhlet (16 hr.) | 303 | 92 |
| 210 | 11 day HCl, Soxhlet (16 hr.) | see Table 2 | |
| 211 | 1 hr. KOH, Soxhlet (16 hr.) | 325 | 89 |
| 212 | 24 hr. KOH, Soxhlet (16 hr.) | 309 | 90 |
| 213 | 3 day KOH, Soxhlet (16 hr.) | 307 | 97 |
| 214 | 7 day KOH, Soxhlet (16 hr.) | 319 | 100 |
| 215 | 11 day KOH, Soxhlet (16 hr.) | 307 | 82 |
| 216 | 1 hr. PEG, Soxhlet (16 hr.) | 332 | 107 |
| 217 | 24 hr. PEG, Soxhlet (16 hr.) | 317 | 95 |
| 218 | 3 day PEG, Soxhlet (16 hr.) | 316 | 116 |
| 219 | 7 day PEG, Soxhlet (16 hr.) | 320 | 94 |
| 220 | 11 day PEG, Soxhlet (16 hr.) | 302 | 91 |
| 221 | 1 hr. after addition of $^{37}Cl$-2,3,7,8-TCDD, Soxhlet (15 hr.) | 317 | 96 |
| 222 | 8 hr. after addition of $^{37}Cl$-2,3,7,8-TCDD, Soxhlet (16 hr.) | 323 | 76 |
| 223 | 24 hr. after addition of $^{37}Cl$-2,3,7,8-TCDD, Soxhlet (16 hr.) | 316 | 92 |
| 224 | 3 days after addition of $^{37}Cl$-2,3,7,8-TCDD, Soxhlet (16 hr.) | 322 | 101 |
| 225 | 7 days after addition of $^{37}Cl$-2,3,7,8-TCDD, Soxhlet (16 hr.) | 317 | 95 |
| 226 | 11 days after addition of $^{37}Cl$-2,3,7,8-TCDD, Soxhlet (16 hr.) | 316 | 83 |
| 227 | Bottle Extraction, no pretreatment | 330 | 91 |
| 228 | Bottle Extraction, no pretreatment | 326 | 89 |

TABLE 5

RESULTS OF REPLICATE ANALYSES OF SOXHLET EXTRACT OF DENNY FARM SOIL

| WSU Sample Number | Concentration of 2,3,7,8-TCDD Found (ng/g) | Percent Recovery of $^{37}Cl$-2,3,7,8-TCDD Internal Standard |
|---|---|---|
| EHK-210-1 | 296 | 92 |
| EHK-210-1 | 289 | 88 |
| EHK-210-3 | 294 | 78 |
| EHK-210-4 | 299 | 84 |
| EHK-210-5 | 294 | 92 |
| EHK-210-6 | 295 | 83 |
| EHK-210-7 | 290 | 83 |
| EHK-210-8 | 293 | 82 |
| EHK-210-9 | 294 | 86 |
| EHK-210-10 | 293 | 82 |
| | $\bar{X}$ = 294 | $\bar{X}$ = 85 |

TABLE 6

RESULTS OF REPLICATE ANALYSES OF BOTTLE EXTRACT OF DENNY FARM SOIL

| WSU Sample Number | Concentration of 2,3,7,8-TCDD Found (ng/g) | Percent Recovery of $^{37}Cl$-2,3,7,8-TCDD Internal Standard |
|---|---|---|
| EHK-229-1 | 312 | 97 |
| EHK-229-2 | 307 | 87 |
| EHK-229-3 | 306 | 73 |
| EHK-229-4 | 309 | 99 |
| EHK-229-5 | 309 | 95 |
| EHK-229-6 | 303 | 96 |
| EHK-229-7 | 311 | 94 |
| EHK-229-8 | 308 | 111 |
| EHK-229-9 | 303 | 90 |
| EHK-229-10 | 302 | 99 |
| | $\bar{X}$ = 307 | $\bar{X}$ = 94 |

TABLE 7

RESULTS OF REPLICATE ANALYSES OF A SINGLE SOIL EXTRACT PERFORMED AT VARIOUS TIME INTERVALS SUBSEQUENT TO EXTRACTION

| WSU Sample Number | Time Elapsed Following Extraction | Concentration of 2,3,7,8-TCDD Found (ng/g) | Percent Recovery of $^{37}Cl$-2,3,7,8-TCDD Internal Standard |
|---|---|---|---|
| EHK-210-1 | 4 days | 297 | 83 |
| EHK-210-2 | 4 days | 289 | 83 |
| EHK-210-3 | 4 days | 296 | 104 |
| EHK-210-4 | 4 days | 296 | 85 |
| EHK-210-5 | 6 days | 302 | 72 |
| EHK-210-6 | 6 days | 298 | 82 |
| EHK-210-7 | 6 days | 303 | 85 |
| EHK-210-8 | 6 days | 297 | 84 |
| EHK-210-9 | 8 days | 297 | 86 |
| EHK-210-10 | 8 days | 296 | 94 |
| EHK-210-11 | 8 days | 299 | 76 |
| EHK-210-12 | 8 days | 293 | 77 |

D. Results of Analyses of "Conditioned" Homogenized Soil

Three 50 gram aliquots of Denny Farm soil were treated by adding to the first, 12 grams of concentrated hydrochloric acid, to the second 12 grams of 40% aqueous potassium hydroxide, and to the third 12 grams of PEG-400. Aliquots of each of the three treated soils were then withdrawn at various time intervals, and each of the aliquots were Soxhlet extracted and analyzed by GS-MS. The analytical results obtained are also shown in Table 4 (Sample Numbers 206-220).

E. Results of Experiment to Assess the Time-Dependence of $^{37}Cl$-2,3,7,8-TCDD Binding to Soil

Fifty grams of homogenized Denny Farm soil were inoculated with five successively applied aliquots of a benzene solution of $^{37}Cl_4$-2,3,7,8-TCDD, in order to obtain a final concentration in the spike sample of 50ng $^{37}Cl_4$-2,3,7,8-TCDD per gram of soil. The sample was vigorously stirred after addition of each aliquot in order to obtain a homogeneously spiked sample. Listed in Table 4 (Sample Numbers 221-226) are the results of the analyses of aliquots of this spiked soil sample, which were obtained at various time intervals following spiking of the soil. The percent recovery obtained for the $^{37}Cl_4$-2,3,7,8-TCDD internal standard in these experiments is indicative of the effect of time on recovery of the added $^{37}Cl_4$-2,3,7,8-TCDD.

The analytical procedures applied in this set of experiments were the same as those described in the original protocol described in Appendix II. The above studies, aimed at defining the factors controlling the precision and accurary of TCDD determinations, indicated that the original analytical procedures were entirely adequate.

## VII. PHASE III TEST SERIES

The data presented in Tables 4, 5, 6 and 7 suggested that soil inhomogeneity was a major factor in the variability of TCDD analytical data experienced in the first series of dehalogenation tests. Consequently, a second series of APEG treatments were initiated on July 21 with more thoroughly homogenized TCDD-contaminated soil samples from Denny Farm. Because of the development of an improved reagent since the start of the original study, the K-120 originally used was replaced with KM-350, i.e., a reagent based on polyethylene glycol monomethylether molecular weight 350. Also, the K-400 reagent used in Phase III was prepared directly from KOH pellets, rather than the 66% aqueous KOH solution used in Phase I. In addition, this test series was conducted with a single bulk batch of soil for each reagent, (in contrast to the first tests where many discrete soil samples were tested with a given reagent) in the interest of reducing the number of variables affecting the measurements. One of the reagents--the K-400--was selected for a double application, i.e., 12 days after the initial application, the same soil sample was treated a second time with the reagent. The experimental protocol for these tests was as follows:

A. Homogenization of Denny Farm Soil Sample

A large bulk sample (at least 1000 grams) of the Denny Farm soil from Missouri, which was previously provided to WSU by EPA, was homogenized in the same manner as just described in Section VI.A. These procedures involved sieving of the soil and collection of the fraction which passes a 4mm mesh screen, followed by mixing and pulverizing the latter fraction in a ceramic ball mill using Bordundum grinding media. The resultant sample was seived again through a 1mm mesh screen and the material passing this sieve was utilized in the experiment initiated on July 21.

B. Preparation and Treatment of Soil Samples

1. Single-Treatment Tests. Five sample vessels were prepared, each containing 100 grams of the homogenized Denny Farm soil. One of these samples was not treated, and served as the control sample. Each of the other three soil samples was subjected to a different reagent by applying 40 milliters of reagent (which was sufficient to completely wet the sample). Immediately following application, the soil and reagent were stirred thoroughly to ensure complete mixing and intimate contact. The stoichiometric ratios of reagents to organochlorine were in the range of 100-300 to 1. Each of the vessels was then tightly covered with aluminum foil and placed in a hood, where the vessels remained until the samples were withdrawn for analyses.

Following application of the reagents, portions of each of the treated and control samples were analyzed for TCDD, as described in Appendix II (results in Table 8).

2. Sequential Treatment Test. One sample vessel containing 100 grams of Denny Farm soil was prepared and utilized for a sequential treatment test. This sample was treated initially with K-400 at the same time as the other samples described in Section VII.B.1. However, in this case, a second application of an equal quantity of K-400 was made twelve days following the initial treatment. Portions of the sample were analyzed in the same manner as the samples discussed above. Results are given in Table 9.

C. Sampling and Analytical Procedures and Schedule

Following treatment of the samples, five-gram aliquots of each of the treated and control samples were withdrawn from the sample vessels and analyzed for 2,3,7,8-TCDD content. This was accomplished according to the schedule defined in Table 10.

TABLE 8

WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435
RESULTS OF TREATING DENNY FARM (MISSOURI) SOIL SAMPLES CONTAMINATED WITH 2,3,7,8-TCDD
WITH SELECTED CHEMICAL REAGENTS - PHASE II

| Time Interval Between Treatment and Analysis | WSU Sample No. | No. Reagent-Control | WSU Sample No. | K-400 | WSU Sample No. | KM-350 |
|---|---|---|---|---|---|---|
| | Concentration of TCDD in Sample (parts-per-billion) | | | | | |
| 1 day | EHK-361 | 300 | EHK-321 | 276 | EHK-341 | 254 |
| 1 day | EHK-362 | 300 | EHK-322 | 277 | EHK-342 | 253 |
| 1 day | EHK-363 | 298 | EHK-323 | 271 | EHK-343 | 251 |
| Average | --- | 299 | --- | 275 | --- | 253 |
| 7 days | EHK-364 | 294 | EHK-324 | 247 | EHK-344 | 208 |
| 7 days | EHK-365 | 315 | EHK-325 | 250 | EHK-345 | 225 |
| 7 days | EHK-366 | 295 | EHK-326 | 231 | EHK-346 | 224 |
| Average | --- | 301 | --- | 243 | --- | 219 |
| 14 days | EHK-367 | 312 | EHK-327 | 261 | EHK-347 | 202 |
| 14 days | EHK-368 | 313 | EHK-328 | 244 | EHK-348 | 200 |
| 14 days | EHK-369 | 318 | EHK-329 | 288 | EHK-349 | 199 |
| Average | --- | 314 | --- | 264 | --- | 200 |
| 21 days | EHK-370 | 303 | EHK-330 | 233 | EHK-350 | 170 |
| 21 days | EHK-371 | 310 | EHK-331 | 224 | EHK-351 | 184 |
| 21 days | EHK-372 | 321 | EHK-332 | 238 | EHK-352 | 182 |
| Average | --- | 311 | --- | 232 | --- | 179 |
| 28 days | EHK-373 | 329 | EHK-333 | 254 | EHK-353 | 180 |
| 28 days | EHK-374 | 312 | EHK-334 | 253 | EHK-354 | 179 |
| 28 days | EHK-375 | 315 | EHK-335 | 240 | EHK-355 | 184 |
| Average | --- | 319 | --- | 249 | --- | 181 |

TABLE 9

WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435

COMPARISON OF RESULTS OF SINGLE AND MULTIPLE TREATMENT OF 2,3,7,8-TCDD CONTAMINATED SOIL FROM DENNY FARM (MISSOURI) WITH K-400 REAGENT

| Single Treatment | | Multiple Treatment[a] | |
|---|---|---|---|
| Time Interval Between Treatment and Analysis | Concentration of TCDD in Soil Sample (parts-per-billion) | Time Interval Between Second Treatment and Analysis | Concentration of TCDD in Soil Sample (parts-per-billion) |
| 14 days | 261 | 14 days | 151 |
| 14 days | 244 | 14 days | 137 |
| 14 days | 288 | 14 days | 126 |
| Average | 264 | Average | 138 |
| 21 days | 233 | 21 days | 109 |
| 21 days | 224 | 21 days | 91 |
| 21 days | 238 | 21 days | 103 |
| Average | 232 | Average | 101 |

[a] 12 days following the initial treatment, the same soil sample was treated a second time.

TABLE 10

EXPERIMENTS TO DETERMINE THE EFFICACY OF SELECTED CHEMICAL REAGENTS FOR DEGRADATION OF 2,3,7,8-TCDD IN SOILS [a]

| Days Between Treatment and Analysis | Soil Conditions/Treatment | | | |
|---|---|---|---|---|
| | Untreated | K-400 | KM-350 | Two Sequential Treatments of K-400 |
| 1 | 3 | 3 | 3 | - |
| 7 | 3 | 3 | 3 | - |
| 14 | 3 | 3 | 3 | 3 |
| 21 | 3 | 3 | 3 | 3 |
| 28 | 3 | 3 | 3 | 3 |
| Total Number of Samples | 15 | 15 | 15 | 9 |

[a] All soil samples treated will be from a single batch of homogenized Denny Farm soil.

## VIII. DISCUSSION AND CONCLUSION

The data of Tables 5 and 6 were analyzed statistically to test (at the 90% confidence level) whether differences exist between exhaustive Soxhlet extraction and the quicker, less-expensive bottle extraction methods. No evidence was found that exhaustive Soxhlet extraction, even with fresh solvent and with extraction times of up to 32 hours, extracts more TCDD than bottle extraction with extraction times of no more than three hours.

A statistical analysis of Table 4 shows that although statistically significant (at the 90% confidence level) differences exist between "unconditioned" and "conditioned" soils (by "conditioning" is meant the addition of HCl, potassium hydroxide or polyethylene glycol of molecular weight 400, i.e., PEG-400, to the soil sample, followed by analysis for TCDD), the size of these differences is relatively unimportant. The following averages, calculated from the data of Table 4, illustrate the differences found:

| | |
|---|---|
| Unconditioned: | 292 ppb TCDD |
| With HCl: | 302 ppb TCDD |
| With KOH: | 313 ppb TCDD |
| With PEG-400: | 317 ppb TCDD |

The existence of a possible time effect in the data of Table 4 was tested by fitting a linear regression model to the above four unconditioned/conditioned data sets and testing the slope for significance. In no case was the slope found to be statistically different from zero (at the 90% confidence level). A similar test was made on the data of Table 4 to see whether there was a time effect with regard to the percent recovery of the internal standard. No such effect was found.

Finally, it should be noted (from Tables 5 and 6) that the precision of extract replicates improved markedly over those originally observed in this study, a matter of about 1% (expressed as a coefficient of variation) in Phase III, compared to the 18% observed in Phase I.

The data of Phase II (the supplementary experiments) and of Phase III strongly suggest: (a) that soil samples be thoroughly homogenized before subjecting them to treatment with APEG reagents in laboratory studies if the objective is to determine the significance of critical variables; and (b) that APEG reagents can, under certain laboratory conditions, significantly reduce the levels of TCDD in contaminated soils.

Although this study has accomplished its proof-of-principle objective, further work must address the following questions:

- What is the toxicological significance of by-products of APEG-dioxin reactions in soils?
- Can additives by found (surfactants, wetting agents, etc.) to increase and accelerate the contact between the reagent and TCDD that is tightly-bound to soil particles and other materials commonly found in soils?

- Are there other processes (radio frequency heating, biological systems, photolysis, etc.) that can enhance the use of APEG reagents on contaminated soils?

- What are the optimal methods for applying APEGs to soils and maintaining the integrity of the site (prevention of water influx, etc.) during the reaction period?

# APPENDIX I

## WEIGHT OF SOIL SAMPLES BEFORE AND AFTER THE ADDITION OF REAGENTS

BREHM LABORATORY, WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435
WEIGHTS OF SOIL SAMPLES BEFORE AND AFTER ADDITION OF
REAGENTS AND WEIGHT OF ALIQUOTS WITHDRAWN FOR ANALYSIS FOR TCDD
VIAR & CO. SAS NO. 362-HQ

| Sample Number | Sample Weight (grams) | Combined Weights of Reagent, Soil (grams) and Covers | Weight of Aliquot Withdrawn For Analysis (grams) |
|---|---|---|---|
| FDE-1 | 50.48 | 75.92 | 6.19 |
| FDE-2 | 50.31 | -- | 5.53 |
| FDE-3 | 50.47 | 79.56 | 6.52 |
| FDE-4 | 50.00 | 77.75 | 6.14 |
| FDE-5 | 50.35 | 80.67 | 5.02 |
| FDE-6 | 49.47 | 80.41 | 4.94 |
| FDE-7 | 50.78 | 83.29 | 7.92 |
| FDE-8 | 50.09 | 79.10 | 6.83 |
| FDE-9 | 49.42 | 82.76 | 7.50 |
| FDE-10 | 49.56 | 80.07 | -- |
| FDE-11 | 50.20 | 79.11 | -- |
| FDE-12 | 50.88 | 77.69 | -- |
| FDE-13 | 50.18 | 76.22 | -- |
| FDE-14 | 50.01 | 86.20 | -- |
| FDE-15 | 50.24 | 80.91 | -- |
| FDE-16 | 50.15 | 78.22 | -- |
| FDE-17 | 49.94 | 75.92 | -- |
| FDE-18 | 50.54 | 82.03 | -- |
| FDE-19 | 49.53 | -- | 3.85 |
| FDE-20 | 49.74 | -- | 5.46 |

| Sample Number | Sample Weight (grams) | Combined Weights of Reagent, Soil (grams) and Covers | Weight of Aliquot Withdrawn For Analysis (grams) |
|---|---|---|---|
| FDE-21 | 49.62 | -- | 5.59 |
| FDE-22 | 50.29 | -- | 5.22 |
| FDE-23 | 49.94 | -- | 5.03 |
| FDE-24 | 50.36 | -- | 5.19 |
| FDE-25 | 50.40 | 101.08 | 8.56 |
| FDE-26 | 49.97 | 78.39 | 6.18 |
| FDE-27 | 50.34 | 77.50 | 6.29 |
| FDE-28 | 50.22 | 76.26 | 5.13 |
| FDE-29 | 50.37 | 80.01 | 5.61 |
| FDE-30 | 50.15 | 76.07 | 5.17 |
| FDE-31 | 50.26 | 82.44 | 7.63 |
| FDE-32 | 50.08 | 78.14 | 8.21 |
| FDE-33 | 50.57 | 82.56 | 6.47 |
| FDE-34 | 50.13 | 80.24 | -- |
| FDE-35 | 50.53 | 78.47 | -- |
| FDE-36 | 50.12 | 78.28 | -- |
| FDE-37 | 50.22 | 76.96 | -- |
| FDE-38 | 50.12 | 77.71 | -- |
| FDE-39 | 50.12 | 77.83 | -- |
| FDE-40 | 50.07 | 80.50 | -- |
| FDE-41 | 50.05 | 81.37 | -- |
| FDE-42 | 50.20 | 75.96 | -- |
| FDE-43 | 49.99 | -- | 5.06 |
| FDE-44 | 49.98 | -- | -- |

| Sample Number | Sample Weight (grams) | Combined Weights of Reagent, Soil (grams) and Covers | Weight of Aliquot Withdrawn For Analysis (grams) |
|---|---|---|---|
| FDE-45 | 50.10 | 77.03 | 6.10 |
| FDE-46 | 50.08 | -- | -- |
| FDE-47 | 50.38 | -- | -- |
| FDE-48 | 50.47 | -- | -- |
| FDE-49 | 50.08 | -- | -- |
| FDE-50 | 50.13 | -- | -- |
| FDE-51 | 55.92 | 85.90 | 7.32 |
| FDE-52 | 50.21 | 85.12 | 6.66 |
| FDE-53 | 50.44 | 83.48 | 6.57 |
| FDE-54 | 50.28 | 84.57 | 5.73 |
| FDE-55 | 50.02 | 83.89 | 5.67 |
| FDE-56 | 50.16 | 85.50 | 5.72 |
| FDE-57 | 50.13 | 82.69 | 5.38 |
| FDE-58 | 50.03 | 83.64 | 5.53 |
| FDE-59 | 50.02 | 82.93 | 5.62 |
| FDE-60 | 49.98 | 85.61 | -- |
| FDE-61 | 50.18 | 78.37 | -- |
| FDE-62 | 50.31 | 83.01 | -- |
| FDE-63 | 50.30 | 93.90 | 7.66 |
| FDE-64 | 50.21 | 91.50 | -- |
| FDE-65 | 50.34 | 91.85 | -- |
| FDE-66 | 50.39 | -- | -- |

| Sample Number | Sample Weight (grams) | Combined Weights of Reagent, Soil (grams) and Covers | Weight of Aliquot Withdrawn For Analysis (grams) |
|---|---|---|---|
| FDE-67 | 50.03 | -- | -- |
| FDE-68 | 50.08 | -- | -- |
| FDE-69 | 50.05 | -- | 5.13 |
| FDE-70 | 50.19 | -- | 5.24 |
| FDE-71 | 50.22 | -- | 5.51 |
| FDE-72 | 50.02 | -- | 5.20 |
| FDE-73 | 50.17 | -- | 4.70 |
| FDE-74 | 50.16 | -- | 5.28 |
| FDE-75 | 50.27 | -- | 5.86 |
| FDE-76 | 50.27 | -- | 6.08 |
| FDE-77 | 50.16 | -- | 5.12 |
| FDE-78 | 50.07 | -- | -- |
| FDE-79 | 50.12 | -- | -- |
| FDE-80 | 50.30 | -- | -- |
| FDE-81 | 50.06 | -- | -- |
| FDE-82 | 50.02 | -- | -- |
| FDE-83 | 50.08 | -- | -- |
| FDE-84 | 50.16 | -- | -- |
| FDE-85 | 50.04 | -- | -- |
| FDE-86 | 50.05 | -- | -- |
| FDE-87 | 50.15 | -- | -- |
| FDE-88 | 50.09 | -- | -- |
| FDE-89 | 50.25 | -- | -- |

| Sample Number | Sample Weight (grams) | Combined Weights of Reagent, Soil (grams) and Covers | Weight of Aliquot Withdrawn For Analysis (grams) |
|---|---|---|---|
| FDE-90 | 50.05 | -- | 5.10 |
| FDE-91 | 50.05 | -- | 5.06 |
| FDE-92 | 50.08 | -- | 5.03 |
| FDE-93 | 50.18 | -- | 5.05 |
| FDE-94 | 50.04 | -- | 5.24 |
| FDE-95 | 50.01 | -- | 5.16 |
| FDE-96 | 50.21 | -- | -- |
| FDE-97 | 50.02 | -- | -- |
| FDE-98 | 50.13 | -- | -- |
| FDE-99 | 50.18 | -- | -- |
| FDE-100 | 50.10 | -- | -- |
| FDE-101 | 50.15 | -- | -- |
| FDE-102 | 50.10 | -- | -- |
| FDE-103 | 50.21 | -- | -- |
| FDE-104 | 50.21 | -- | -- |
| FDE-105 | 50.30 | -- | -- |
| FDE-106 | 50.04 | -- | -- |
| FDE-107 | 50.03 | -- | 5.80 |
| FDE-124 | 49.48 | -- | 5.09 |
| FDE-125 | 50.20 | -- | 5.03 |
| FDE-126 | 50.52 | -- | 5.09 |
| FDE-127 | 50.17 | -- | 5.12 |
| FDE-128 | 49.94 | -- | 5.10 |

| Sample Number | Sample Weight (grams) | Combined Weights of Reagent, Soil (grams) and Covers | Weight of Aliquot Withdrawn For Analysis (grams) |
|---|---|---|---|
| FDE-129 | 50.72 | -- | 5.08 |
| FDE-130 | 49.49 | -- | 5.35 |
| FDE-131 | 49.56 | -- | -- |
| FDE-132 | 50.36 | -- | -- |

# APPENDIX II

## EXPERIMENTAL PROTOCOL FOR TESTS OF THE EFFICACY OF APEG REAGENTS FOR DESTRUCTION OF 2,3,7,8-TCDD IN CONTAMINATED SOIL SAMPLES

## I. SCOPE OF PROTOCOL

The U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Cincinnati, Ohio [EPA/IERL (Cinn.)] plans to conduct a series of tests, in conjunction with the Brehm Laboratory of Wright State University, Dayton, Ohio, to evaluate the capabilities of a previously developed chemical reagent, KPEG, for degradation of 2,3,7,8-TCDD which is present as a contaminant in selected soil samples. The proposed tests will be conducted at the Brehm Laboratory and the soils to be tested will be representative samples collected from TCDD-contaminated horse arenas and/or related sites located in the State of Missouri. The soil samples to be tested will be provided by EPA/Region VII (Kansas City). The experimental protocol presented here describes the procedures which will be employed in 1) preparing soil samples, 2) treating these with the KPEG reagent, 3) analyzing the soil samples (before and following treatment) to determine the concentrations of 2,3,7,8-TCDD contained therein, and 4) analyzing a few of the soil samples to identify other chemical compounds which are present, especially other chlorinated hydrocarbons, including other chlorodibenzo-p-dioxins (CDDs) and/or chlorodibenzofurans (CDFs).

## II. PREPARATION OF SOIL SAMPLES FOR TREATMENT

Two (2) bulk batches of soil, consisting of ten (10) kilograms each of soil from two representative Missouri sites, will be collected by EPA/Region VII and provided to the Brehm Laboratory for use in the tests. Upon receipt, these samples will be prepared by the Brehm Laboratory according to the procedures described below.

A. Homogenization of Bulk Soil Samples

Upon receipt of the soil samples, each 10 kilogram portion will be separately transferred to a glove-box where the batches of soil will be screened, using a 4mm mesh-size sieve, to remove stones and other foreign matter. The sieved soils will then be stirred vigorously (in smaller batches, which will be recombined) to homogenize each batch. Portions of each of these homogeneous bulk samples will then be used for the TCDD destruction tests.

B. Treatment of Simulated Soil

As an initial test, it is appropriate to determine directly the capability of the KPEG reagent to degrade 2,3,7,8-TCDD. Since previous EPA-sponsored tests of the dechlorinating ability of this reagent, which were conducted on PCBs and other chlorinated hydrocarbons, involved the use of glass beads to simulate soils, it is planned to conduct a similar test with 2,3,7,8-TCDD. A 50-gram quantity of 1-mm. diameter glass beads will be spiked with 2,3,7,8-TCDD by immersing the beads in an appropriate quantity of a benzene solution of this compound and then evaporating off the solvent by applying mild heat and passing a stream of dry nitrogen over the beads. The TCDD spiked beads will then be treated with the KPEG reagent by adding an appropriate quantity of the reagent (typically in a quantity corresponding to a ten-fold excess of reagent to TCDD - this is discussed further below). Aliquots of the 2,3,7,8-TCDD spiked glass beads will be analyzed to determine the actual 2,3,7,8-TCDD concentration both before and after treatment of these with the KPEG reagent. This will provide an indication of the dechlorinating capability of the reagent for TCDD. If the TCDD content has been reduced by the treatment, then other samples of the treated glass beads will also be analyzed for other chlorodibenzodioxins

and possibly chlorodibenzofurans, in order to determine if products resulting from partial dechlorination or rearrangement reactions have been formed. A screening analysis will also be conducted in an effort to determine other products of the reaction.

It may also be useful to directly treat a solution of 2,3,7,8-TCDD (not sorbed on any surface) with the KPEG reagent in the initial phase of this study.

C. Preparation of Soil Test Vessels and Treatment With KPEG

Fifty-(50) gram aliquots of each of the two soils to be tested will be removed from the homogenized batches and transferred to 150 mL beakers (5.5 cm. diameter x 8 cm. in height). This will yield soil test vessels in which the depth of soil is approximately 0.75 to 1 inch. One hundred and two (102) of these vessels will be prepared and clearly labelled with identifying information. Some of these soil aliquots will be treated with the KPEG reagent and some, which will not be treated, will serve as control samples. The sample vessels will be covered loosely with aluminum foil, to prevent any cross contamination, and placed in a closed self-contained hood, which is designed for handling toxic materials, and which uses a fully filtered air supply (both intake and exhaust air). The sample vessels will be kept in these hoods throughout the duration of the tests.

Scientists from EPA/IERL (Cinn.) will prepare an appropriate quantity of the KPEG reagent and will use this to treat the soil samples at the Brehm Laboratory test site. This will be accomplished by carefully spraying a known predetermined amount of the reagent into each of the beakers containing

soils to be tested. The beakers will be weighed accurately by Brehm Lab personnel at three different points in the tests, a) at the time when the soils are placed in the vessels, b) immediately following addition of the reagent (for those beakers which are treated) and c) just prior to analysis of the soil in each beaker. This is necessary in order to take into account the possible loss of water from the soil samples which may occur during the tests. Following addition of the KPEG reagent to those beakers in which the degradation efficiency is to be tested, the soil and reagent in each vessel will be gently stirred with a spatula to ensure intimate contact, and the vessels will immediately be covered with foil and placed in the hoods. The vessels will be at ambient or room temperature throughout the tests.

The quantity of reagent to be added to the test soils will be determined on the basis of preliminary determinations of the total organic chlorine content in each of the two bulk soil batches. The procedures for these determinations are described in the section on analytical methods. The KPEG reagent will be added to the soil samples in quantities such that there is a ten-fold excess of KPEG with respect to total organic chlorine on a molar basis. In the preliminary analyses of the soils, the water content in each of the two bulk soil batches will also be determined, using procedures described in a later section.

At appropriate time intervals following treatment of the soils with KPEG, as shown in the attached Table 1, portions of the beakers containing the treated and control soils will be removed from the hood, and aliquots of the soils will be removed and analyzed for 2,3,7,8-TCDD. The time intervals

shown in Table 1 may be adjusted somewhat, depending upon the observed rate of degradation of TCDD. Obviously, if the reagent is found to degrade virtually all of the TCDD in the first week, then the experiments will not continue over the full thirty days indicated in Table 1. Similarly, if the action of the reagent proves to be measurable, but slow, then the duration of the tests may need to be extended.

If the reagent proves to be effective in reducing the concentration of 2,3,7,8-TCDD in the soils, then it will be appropriate to also analyze a few of the samples in which the TCDD has been significantly reduced for other chlorodibenzodioxins (CDDs) and possibly for chlorodibenzofurans (CDFs). It is anticipated that complete screening for CDDs and CDFs would be accomplished on about eight samples.

Since chlorinated compounds other than TCDD are undoubtedly present in the samples (previous analyses has shown this), it will also be appropriate to screen a few soil samples, both before and after treatment with the reagent, in an effort to identify other chemical compounds which are present. It is expected that such GC-MS screening would be accomplished on about four samples.

## III. ANALYTICAL PROCEDURES

The analytical procedures which will be used in this study are outlined below.

### A. Determination of 2,3,7,8-TCDD

1. Extraction of Soils and Preliminary Fractionation of Extracts.

   a. Weigh a 20 gram aliquot of soil into a 125 mL flint glass bottle

fitted with a Teflon lined cap. Add an appropriate quantity of $^{37}Cl_4$-2,3,7,8-TCDD to the sample (typically 50ng) which is utilized as an internal standard.

b. Extract the soil by adding 10 mL of methanol, followed by 40 mL of hexane to the sample bottle, place the sealed bottle on a wrist action shaker, and agitate the bottle for 3 hours. Remove the bottle and allow it to stand for a period sufficient for the suspended solids to settle.

c. Remove the organic phase and quantitatively transfer it to a clean 250 mL flint glass bottle fitted with a Teflon lined cap.

d. Wash the organic extract with 30 mL of 20% aqueous potassium hydroxide by shaking for 10 minutes and then remove and discard the aqueous layer.

e. Wash the organic extract with 25 mL of doubly distilled water by shaking for 2 minutes and again remove and discard the aqueous layer.

f. Cautiously add 50 mL concentrated sulfuric acid to the organic extract and shake for 10 minutes. Allow the mixture to stand until the aqueous and organic layers separate (~10 minutes) and remove and discard the aqueous acid layer. Repeat acid washing until no color is visible in the acid layer.

g. Add 25 mL of doubly distilled water to the organic extract and shake for 2 minutes, remove and discard the aqueous layer and dry the organic layer by adding 10g of anhydrous sodium sulfate.

h. Transfer the organic extract to a centrifuge tube and concentrate to near dryness by placing the tube in a water bath at 55°C, while passing a gentle stream of filtered, prepurified $N_2$ over the surface of the extract.

i. Prepare a glass macro-column, 20 mm OD x 230 mm in length, tapered to 9mm OD on one end. Pack the column with a plug of silanized glass wool, followed successively by 1.0g silica, 2.0 g silica containing 33% (w/w) 1M NaOH, 1.0 g silica, 4.0g silica containing 44% (w/w) concentrated $H_2SO_4$ and

2.0g silica. Quantitatively transfer the concentrated extract from Step h. to the column and elute with 45 mL hexane. Collect the entire eluate and concentrate to a volume of >1 mL in a centrifuge tube, as before.

j. Construct a chromatography column by packing a 5 mL disposable pipet (cut off at the 2.0 mL mark) with a plug of silanized glass wool and add 1 gram of activated Woelm basic alumina (activated at 600°C for 24 hours) to the tube.

k. Quantitatively transfer the concentrated extract from Step i. to the top of the column using 2 mL hexane.

l. Elute the column with 5 mL of 3% methylene chloride-in-hexane and retain the entire column eluate for analysis.

m. Elute each column with 20 mL of 50% methylene chloride-in hexane and retain the entire column eluate for analysis.

n. Concentrate the eluate to a volume <1 mL and quantitatively transfer it to a Reacti-vial.

o. Further concentrate the extract in the Reacti-vial to near dryness, and store the extract at 5°C until just prior to GC-MS analysis.

p. Prior to GC-MS analysis, reconstitute the extract by adding an appropriate quantity of the desired solvent.

2. Analysis of Sample Extracts Using Coupled High Resolution (Capillary-Column) Gas Chromatography-Low Resolution Mass Spectrometry.

The concentrations of 2,3,7,8-TCDD in the sample extracts are determined by injecting aliquots (typically 10 microliters) of each aliquot into a coupled high resolution (capillary column) gas chromatograph - low resolution mass spectrometer (HRGC-LRMS). The instrument used for these determinations and the operating parameters are as follows.

a. Instrumentation: Perkin Elmer Sigma III Gas Chromatograph coupled through a custom-fabricated interface including a single-stage glass jet separator to a Kratos MS-25 Mass Spectrometer equipped with a DS-50SM Data System. Make up gas was Helium.

b. Conditions for the Gas Chromatograph:

1) Column: 60m WCOT Fused Silica Capillary (SP.2340, 0.25mm ID, Film thickness 0.02mm).

2) Carrier Gas: Hydrogen, 30 lb head pressure.

3) Column Temperature: Isothermal at 190°C for 2 minutes, programmed at 5°C/min from 190°C to 220°C for 17 min., then program at 5°C/min to 230°C, hold at 230°C for 23 min., then program at 5°C/min to 235°C, hold at 235°C for 78 min.

4) Interface Temperature: 250°C

5) Injector Mode: "Grob" Style Splitless Injection

6) Injection Port Temperature: 300°C

c. Conditions for the Mass Spectrometer:

1) Selected Ion Monitoring Mode: m/z's monitored are m/z 320, 322, for 2,3,7,8-TCDD; m/z 328 for $^{37}Cl_4$-2,3,7,8-TCDD; and m/z 332 for $^{13}C_{12}$-2,3,7,8-TCDD.

2) Ionizing Voltage: 70 eV

3) Accelerating Voltage: 4 KV

4) Resolution: 1:1000

3. Reagents and Chemicals.

The following is a listing of the reagents and chemicals utilized in the procedures outlined above. Potassium hydroxide, anhydrous sodium sulfate, and sulfuric acid were all Reagent Grade and were obtained from J.T. Baker Chemical Co. or Fisher Scientific Co., Fairlawn, N.J. Methanol, hexane, methylene chloride and benzene were "Distilled in Glass" quality obtained from Durdick

and Jackson, Muskegon, Michigan. Woelm basic alumina (Activity Grade I) was obtained from ICN Pharmaceuticals, Cleveland, Ohio. Silica (Bio-Sil A) was obtained from Bio-Rad, Rockville Centre, New York. Doubly distilled water was obtained using the all-glass distillation apparatus in the Brehm Laboratory. Prepurified nitrogen was obtained from Airco, Inc., Montvale, New Jersey.

Standards employed in this work were obtained from:

a. $^{37}Cl_4$-2,3,7,8-TCDD and $^{13}C_{12}$-2,3,7,8-TCDD: KOR Isotopes, Cambridge, Mass.
b. All 22 TCDD Isomers obtained from Brehm Laboratory, Dow Chemical Co., Midland, Michigan, and H.R. Buser,Swiss Federal Research Station, Wadenswil, Switzerland.

4. Calibration of GC-MS and Determination of TCDD Concentration

The GC-MS system is calibrated by injecting authentic standards, in appropriate concentrations (spanning the range of interest), of 2,3,7,8-TCDD, $^{37}Cl_4$-2,3,7,8-TCDD and $^{13}C_{12}$-2,3,7,8-TCDD. Response factors at the appropriate ion masses used to monitor each of these compounds (m/z 320, 322, 328, 332) are obtained. The data system of the MS automatically determines peak heights for the appropriate ions, both for the calibration standards and the extracts of samples being analyzed. The concentrations of 2,3,7,8-TCDD in the samples are calculated by obtaining the ratios of the peak heights for the native TCDD indicators (m/z 320, 322) to those for the internal standards (m/z 328, 332) and applying the measured response factors. The $^{37}Cl_4$-2,3,7,8-TCDD is added to each sample prior to extraction and serves as an overall recovery indicator. The $^{13}C$-2,3,7,8-TCDD is coinjected with the sample extract to provide an indicator of instrument sensitivity variations. The measured ratio of the chlorine isotope peaks, for the sample extracts, as indicated by the m/z 320 to m/z 322 ratio, must generally be within 10% of that observed for the native TCDD standard to confirm the presence of TCDD.

5. Quality Assurance

Quality assurance for the analyses is provided principally by the use of an isotopically labelled internal standard (either $^{37}Cl_4$-2,3,7,8-TCDD or $^{13}C_{12}$-2,3,7,8-TCDD) which is added in known quantity to each sample prior to extraction and analysis. This labelled TCDD is quantitatively measured simultaneously with the native TCDD in the sample and the percent recovery of the labelled TCDD serves as an indicator of the efficacy of the methodology and of each particular analysis. The minimum acceptable recovery of the labelled TCDD is 25%. Procedural blank samples are also analyzed routinely (typically one blank for each 10-20 analyses) along with the actual samples. In the present study, each sample type (corresponding to a given treatment experiment) will be analyzed in triplicate (see Table 1) to ensure reliable results.

B. Determination of Other CDDs and CDFs

The extraction and cleanup procedures applied to screen samples for the entire series of CDDs and CDFs (mono- through octachlorinated) are quite similar to those already described in the analytical method for TCDD. In this case, however, additional internal standards are added, including $^{37}Cl_4$-Hepta CDD and $^{37}Cl_8$-OCDD. A slightly different liquid chromatography elution procedure is also applied to obtain all CDDs and CDFs in a single extract.

The GC-MS procedures applied to determine the entire series of CDDs and CDFs in the sample extracts are shown in Table 2, which indicates both the chromatographic sequence (a 50 meter OV-101 WCOT capillary column is used) and the selected ion monitoring sequences applied.

C. Determination of Total Organic Chlorine

Total organic chlorine in the samples will be determined by using a method provided in the EPA Manual of Chemical Methods for Pesticides. A copy of this procedure is included herewith.

D. Screening of Sample Extracts for Other Compounds

The extraction and analytical methodology described in EPA Method 625, Analysis of Priority Pollutants will be generally followed in the screening determinations. However, interpretation of the mass spectra of the various components will be accomplished both by computer matching with mass spectral lib-aries and manual reduction and identification. Our experience with similar samples from the Missouri area suggests that this will be necessary.

## IV. NUMBERS OF ANALYSES

The total numbers of analyses of samples expected to be required in connection with the test program described above are summarized below. As already noted, this may be subject to adjustment, depending upon the outcome of the experiments.

A. Maximum Number of Analyses For 2,3,7,8-TCDD = 102

B. Number of Analyses For CDDs/CDFs (mono- through octachlorinated) = 8

C. Number of Analyses For Total Organic Chlorine = 4

D. Number of Screening Analyses For Other Compounds = 4

## V. SAFETY

The Brehm Laboratory of Wright State University has extensive experience in the handling of highly toxic compounds such as the chlorodibenzodioxins and chlorodibenzofurans, as a consequence of some ten years of research and development relating to these compounds. The Laboratory has been and continues to be engaged in numerous analytical, synthetic and degradation studies relevant to these compounds, and this work is supported by EPA, the U.S. Air Force, and numerous industrial firms. The formal safety protocols developed and utilized routinely by the Brehm Laboratory in the course of all such studies will be rigorously followed in the work proposed here. The planned studies will be conducted in controlled access, safe labs, and only highly experienced scientific personnel will be associated with this project. Details of the Brehm Lab safety protocols and personnel monitoring programs utilized in dioxin related projects have been previously provided to EPA.

TABLE 1

EXPERIMENTS TO DETERMINE THE EFFICACY OF APEG FOR THE DEHALOGENATION OF 2,3,7,8-TCDD IN SOILS

| NUMBER OF DAYS FOLLOWING TREATMENT BEFORE ANALYSIS | SOIL A (TIMBERLINE STABLES) NUMBERS OF SAMPLES | | SOIL B (DENNY FARM) NUMBER OF SAMPLES | | | TOTAL SAMPLES |
|---|---|---|---|---|---|---|
| | UNTREATED (CONTROLS) | K-400 TREATED | UNTREATED (CONTROLS) | K-400 TREATED | K-120 TREATED | |
| 0 | 3,3* | 3 | 3,3* | 3 | 3 | 21 |
| 6 | 3 | 3 | 3 | 3 | 3 | 15 |
| 12 | 3 | 3 | 3 | 3 | 3 | 15 |
| 18 | 3 | 3 | 3 | 3 | 3 | 15 |
| 24 | 3 | 3 | 3 | 3 | 3 | 15 |
| 30 | 3,3* | 3 | 3,3* | 3 | 3 | 21 |
| TOTAL NUMBER OF SAMPLES | 24 | 18 | 24 | 18 | 18 | 102 |

*These samples will be spiked with $^{37}Cl_4$-2,3,7,8-TCDD to determine if the binding affinity of the soils for TCDD changes as a function of time.

TABLE 2

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SEQUENCE OF OPERATIONS IN GC-MS (MS-25) ANALYSES OF CHLORODIBENZODIOXINS AND CHLORODIBENZOFURANS IN SAMPLE EXTRACT

| Elapsed Time (min) | Event | GC Column Temperature | Temperature Program Rate ( °C/Min) | Ions Monitored By Mass Spectrometer (m/z) | Compounds Monitored |
|---|---|---|---|---|---|
| 0.00 | Injection, splitless | 190° | -- | | |
| 1.50 | Turn on split valve | 190° | -- | | |
| 2.00 | Begin temp. program to 220°C | 190°C | 5°C/min | | |
| 5.00 | Open Column Flow to Mass Spec. | 202°C | 5°C/min | | |
| 6.50 | Start PROGRAM #2 | | | | |
| | Sweep = 200 ppm | 220°C | -- | 189.010 | $Cl_2$ dioxins |
| | Time on Cl mass = 0.12 sec | | | 235.980 | $Cl_2$ furans |
| | | | | 237.977 | $Cl_2$ furans |
| | | | | 251.974 | $Cl_2$ dioxins |
| | | | | 253.972 | $Cl_2$ dioxins |
| 10.50 | Stop PROGRAM #2 | 220°C | -- | | |
| 11.00 | Start PROGRAM #3 | 220°C | -- | 222.976 | $Cl_3$ dioxins |
| | Sweep = 200 ppm | | | 269.941 | $Cl_3$ furans |
| | Time on Cl mass = 0.12 sec | | | 271.938 | $Cl_3$ furans |
| | | | | 285.935 | $Cl_3$ dioxins |
| | | | | 287.932 | $Cl_3$ dioxins |
| 15.00 | Stop PROGRAM #3 | 220°C | -- | | |
| 15.50 | Start | 220°C | -- | 258.930 | $Cl_4$ dioxins |
| | | | | 303.902 | $Cl_4$ furans |
| | | | | 305.899 | $Cl_4$ furans |
| | | | | 319.897 | $Cl_4$ dioxins |
| | | | | 321.894 | $Cl_4$ dioxins |
| | | | | 327.885 | $^{37}Cl_4$ labelled TCDD |
| 23.50 | Stop PROGRAM #4 | 220°C | -- | | |
| 24.00 | Start PROGRAM #5 | 220°C | -- | 337.863 | $Cl_5$ furans |
| | Sweep = 750 ppm | | | 339.860 | $Cl_5$ furans |
| | Time on penta mass = 0.2 sec | | | 353.858 | $Cl_5$ dioxins |
| | | | | 355.855 | $Cl_5$ dioxins |

Table 2 (cont.)

| Elapsed Time | Event | GC Column Temperature | Temperature Program Rate ( °C/Min) | Ion Monitored By Mass Spectrometer (m/z) | Compounds Monitored |
|---|---|---|---|---|---|
| 25.00 | Begin temp program to 230°C | 220°C | 5°C/Min | | |
| 34.50 | Stop PROGRAM #5 | | | | |
| 35.00 | Start PROGRAM #6 | 230°C | | 373.821 | Cl furans |
| | Sweep = 150 ppm | | | 375.818 | Cl furans |
| | Time on each mass = .25 sec | | | 389.816 | Cl dioxins |
| | | | | 391.813 | Cl dioxins |
| 50.00 | Begin temp program to 235°C | | 5°C/Min | | |
| 53.50 | Stop PROGRAM #6 | 235°C | -- | | |
| 54.00 | Start PROGRAM #7 | 235°C | -- | 407.782 | Cl furans |
| | Sweep = 750 ppm | | | 409.779 | Cl furans |
| | Time on each mass = 0.35 sec | | | 423.777 | Cl dioxins |
| | | | | 425.774 | Cl dioxins |
| | | | | 431.765 | $^{37}$Cl, labelled HpCl |
| 70.00 | Stop PROGRAM #7 | | | | |
| 85.00 | Start PROGRAM #8 | 235°C | -- | 441.732 | Cl furans |
| | Sweep = 750 ppm | | | 443.740 | Cl dioxins |
| | Time on each mass = 0.50 sec | | | 457.738 | Cl dioxins |
| 95.00 | Stop PROGRAM #8 | 235°C | | 459.735 | Cl dioxins |
| 130.00 | Return to initial temp. | | | 471.717 | $^{37}$Cl, labelled OCD |

# APPENDIX III

## EPA PROCEDURE FOR TOTAL ORGANIC CHLORINE DETERMINATION

## Determination of Chlorophenols by the Total Chloride Lime Fusion Method

For definition, structure, and technical data on chlorophenols, see Phenols and Chlorophenols EPA-1.

Principle of the Method:

The method was developed primarily for pentachlorophenol in oil solutions; however, it may be used for other chlorinated phenols. It is not applicable to samples containing other halogens unless these halogens can be determined and appropriate corrections made. This method is based on destroying organic material by heating and absorbing the liberated hydrochloric acid in calcium hydroxide. The hydroxide is neutralized with nitric acid and the chloride determined potentiometrically. Organic matter should be limited to 2 grams and the chlorinated phenol to 35 mg in terms of chlorine.

Reagents:

1. Fusion mixture - 9 parts calcium hydroxide powder plus 1 part potassium nitrate powder, thoroughly mixed. (see note below)
2. Nitric acid, concentrated, ACS
3. Silver nitrate, 0.1N standardized solution

Note: All reagents should be virtually chloride-free. ACS specifications should meet this requirement; however, for greatest accuracy a blank on all reagents should be run using the same amounts and method as for the sample.

4. Phenolphthalein indicator solution

Equipment:

1. Potentiometric titrimeter equipped with a glass reference electrode and a silver electrode
2. Iron crucible, 100 ml capacity, with cover
3. Meker burner, adjustable from minimum air to maximum air
4. Tripod stand and metal triangle (to hold crucible)
5. Ice bath
6. Magnetic stirrer
7. Usual laboratory glassware

Determination:

Place 100 grams of the calcium hydroxide-potassium nitrate mixture in a 100 ml iron crucible, tap gently to settle the contents, and form a small depression with the round bottom of a test tube. From a weighing burette add a weight of sample equivalent to 0.035 gram chlorine. (Solid samples may be mixed with a little fusion mixture and placed in the depression.)

Place 20 grams of the fusion mixture over the sample in the crucible and tap gently on a hard surface to settle and evenly distribute the fusion mixture. It is essential that the fusion mixture be uniformly packed (settled) so that no air pockets are present and thorough and even heating results.

The crucible with cover (to suppress burning of volatile materials on the surface of the fusion mixture) should be placed in a metal triangle on a ring stand so that the bottom is one-half inch above the top of a Meker burner. With the air supply almost completely shut off

and using a very luminous flame, the crucible is heated for about 15 minutes, allowing the flame to completely engulf the crucible all around. Gradually increase the flame temperature (increase the air) to maximum over the next ten minutes until the bottom of the crucible is red hot. Heat at full heat for at least 30 minutes. Samples should be free of unburned carbon; however, a small amount usually presents no errors. Surface should be free of large cracks.

Cool the crucible until it can be handled, then empty the contents into a 600 ml beaker, scraping any adhering fusion mixture into the beaker. Cautiously add about 100 ml water to the beaker and rinse the crucible with small portions of water into the beaker. Place the beaker in an ice bath in a glass dish on a magnetic stirrer. Put a glass or teflon-coated stirring bar and a few drops of phenolphthalein in the beaker and cover with a watchglass. While stirring, cautiously and slowly pour sufficient conc. nitric acid (50 to 60 ml) slowly down the side of the beaker to neutralize the sodium carbonate (keep the beaker covered as much as possible with the watchglass). Cool, and determine the chloride content potentiometrically, titrating with 0.1N silver nitrate solution. A blank should be run on each new batch of fusion mixture and with each change of reagent. Corrections in calculation should be made (usually about 0.05-0.06 ml silver nitrate solution subtracted from the ml silver nitrate used for the sample titration).

**Calculations:**

Calculate the percent chlorine and chlorinated phenol as follows:

$$\% \text{ chlorine} = \frac{(\text{net ml } AgNO_3)(N\ AgNO_3)(0.03545)(100)}{(\text{gram sample})}$$

(0.03545 = milliequivalent weight of chlorine)

% Chlorinated phenol = % chlorine X factor Cl to chlorinated phenol

# APPENDIX IV

## DETAILED ANALYSIS DATA ON AEPG TREATMENT OF TCDD CONTAMINATED SOIL SAMPLES

TABLE 1

RESULTS OF HRGC-LRMS ANALYSES OF EXTRACTS OF EPA/CINN. (IERL) SAMPLES UNDER VIAR & COMPANY SAS NO. 362-HQ FOR 2,3,7,8-TETRACHLORODIBENZO-P-DIOXIN (TCDD)

| WSU Sample No. | Sample Identification | Concentration of 2,3,7,8-TCDD Found (ng./g.) | Observable Signal Response 320,322,257 | Ratio Intensities 320/322 | % of Recovery $^{37}Cl_4$-2,3,7,8-TCDD Internal Standard |
|---|---|---|---|---|---|
| FDE-10 | Timberline, K-120 (21 days) | 214 | Yes | 0.78 | 77 |
| FDE-11 | Timberline, K-120 (21 days) | 210 | Yes | 0.78 | 95 |
| FDE-12 | Timberline, K-120 (21 days) | 248 | Yes | 0.76 | 114 |
| FDE-13 | Timberline, K-120 (28 days) | 179 (177)[a] | Yes | 0.74 | 75 |
| FDE-14 | Timberline, K-120 (28 days) | 170 | Yes | 0.87 | 78 |
| FDE-15 | Timberline, K-120 (28 days) | 167 | Yes | 0.79 | 119 |
| FDE-34 | Timberline, K-400 (21 days) | 220 (223)[a] | Yes | 0.78 | 92 |
| FDE-35 | Timberline, K-400 (21 days) | 224 | Yes | 0.76 | 95 |
| FDE-36 | Timberline, K-400 (21 days) | 220 | Yes | 0.75 | 81 |
| FDE-37 | Timberline, K-400 (28 days) | 170 | Yes | 0.76 | 99 |
| FDE-38 | Timberline, K-400 (28 days) | 196 | Yes | 0.77 | 96 |
| FDE-39 | Timberline, K-400 (28 days) | 172 | Yes | 0.80 | 100 |
| FDE-44 | Timberline, Control (28 days) | 202 | Yes | 0.82 | 58 |
| FDE-48 | Timberline, Control (21 days) | 299 | Yes | 0.78 | 99 |
| FDE-49 | Timberline, Control (21 days) | 273 | Yes | 0.78 | 91 |
| FDE-50 | Timberline, Control (21 days) | 263 | Yes | 0.80 | 95 |
| FDE-129 | Timberline, Control (21 days) | 245 | Yes | 0.80 | 68 |
| FDE-60 | Denny Farm, K-120 (21 days) | 217 | Yes | 0.83 | 55 |
| FDE-61 | Denny Farm, K-120 (21 days) | 350 | Yes | 0.76 | 97 |
| FDE-62 | Denny Farm, K-120 (21 days) | 260 | Yes | 0.78 | 97 |
| FDE-63B | Denny Farm, K-120 (28 days) | 315 | Yes | 0.77 | 63 |
| FDE-64A | Denny Farm, K-400 (21 days) | 353 | Yes | 0.76 | 86 |
| FDE-65A | Denny Farm, K-400 (21 days) | 409 | Yes | 0.76 | 68 |
| FDE-63B | Denny Farm, K-400 (21 days) | 359 | Yes | 0.80 | 105 |

TABLE 1 - Cont.

RESULTS OF HRGC-LRMS ANALYSES OF EXTRACTS OF EPA/CINN. (IERL) SAMPLES UNDER YIAR & COMPANY SAS NO. 362-HQ FOR 2,3,7,8-TETRACHLORODIBENZO-p-DIOXIN (TCDD)

| WSU Sample No. | Sample Identification | Concentration of 2,3,7,8-TCDD Found (ng./g.) | Observable Signal Response 320,322,257 | Ratio Intensities 320/322 | % of Recovery Cl -2,3,7,8-TCDD Internal Standard |
|---|---|---|---|---|---|
| FDE-63C | Denny Farm, K-400 (28 days) | 323 | Yes | 0.80 | 75 |
| FDE-64B | Denny Farm, K-400 (28 days) | 259 | Yes | 0.76 | 75 |
| FDE-78 | Denny Farm, Control (21 days) | 372 | Yes | 0.78 | 75 |
| FDE-79 | Denny Farm, Control (21 days) | 444 | Yes | 0.78 | 69 |
| FDE-80 | Denny Farm, Control (21 days) | 349 | Yes | 0.73 | 95 |
| FDE-90 | Denny Farm, Control (21 days) | 352 | Yes | 0.77 | 87 |
| FDE-83 | Denny Farm, Control (28 days) | 336 | Yes | 0.76 | 80 |
| FDE-91 | Denny Farm, Control (28 days) | 492 | Yes | 0.78 | 70 |
| FDE-93 | Denny Farm, Control (28 days) | 377 | Yes | 0.77 | 66 |

a. Replicate GC-MS analysis of same sample extract.

TABLE 2

BREHM LABORATORY, WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435

TIMBERLINE STABLES SOIL SAMPLES - SUMMARY OF 21-DAY AND 28-DAY TREATMENT TESTS

| Sample Identification | Samples Nos. | TCDD Concentration (ng./g.) | Average TCDD Concentration (ng./g.) |
|---|---|---|---|
| Timberline Stables, Control Samples | FDE-44, -48, -49, -50,-129 | 202, 299, 273, 263, 245 | 256 |
| Timberline Stables, K-120 Treated (21 days) | FDE-10, -11, -12 | 214, 210, 248 | 224 |
| Timberline Stables K-120 Treated (28 days) | FDE-13, -14, -15 | 179, 170, 167 | 172 |
| Timberline Stables K-400 Treated (21 days) | FDE-34, -35, -36 | 220, 224, 220 | 221 |
| Timberline Stables K-400 Treated (28 days) | FDE-37, -38, -39 | 170, 196, 172 | 179 |

TABLE 3

BREHM LABORATORY, WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435

DENNY FARM SOIL SAMPLES - SUMMARY OF 21-DAY AND 28-DAY TREATMENT TESTS

| Sample Identification | Sample Nos. | TCDD Concentration (ng./g.) | Average TCDD Concentration (ng./g.) |
|---|---|---|---|
| Denny Farm, Control Samples | FDE-78, -79, -80, -90, -63, -91, -93 | 372, 444, 349, 352, 336, 492, 377 | 389 |
| Denny Farm, K-120 Treated (21 days) | FDE-60, -61, -62 | 217, 350, 260 | 276 |
| Denny Farm, K-120 Treated (28 days) | FDE-53B | 315 | 315 |
| Denny Farm, K-400 Treated (21 days) | FDE-64A, -65A, -63B | 353, 409, 359 | 374 |
| Denny Farm, K-400 Treated (28 days) | FDE-63C, -64B | 323, 259 | 291 |

TABLE 4

BRENM LABORATORY, WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435

RESULTS OF HRGC-LRMS ANALYSES OF EXTRACTS OF EPA/CINN. (IERL) SAMPLES UNDER VIAR & COMPANY SAS NO. 362-HQ FOR 2,3,7,8-TETRACHLORODIBENZO-p-DIOXIN (TCDD)

| WSU Sample No. | Sample Identification | Concentration of 2,3,7,8-TCDD Found (nanograms TCDD/grams of sample)[a,b] | Observable Signal Response m/z 320 | m/z 322 | m/z 257 | Ratio of Intensities m/z 320 / m/z 322 | % Recovery of $^{37}Cl_4$-2,3,7 TCDD Internal Standard | Date Sample Quenched | Date Sample Extracted | Date Sample Analyzed on GC-MS |
|---|---|---|---|---|---|---|---|---|---|---|
| FDE-23 | Timberline Stables Control Sample (1 day) | 238 (278) | Yes | Yes | Yes | 0.78 | 69 | 12/16/82 | 12/17-12/19/82 | 12/22/82 |
| FDE-24 | Timberline Stables Control Sample (1 day) | 216 | Yes | Yes | Yes | 0.80 | 81 | 12/16/82 | 12/17-12/18/82 | 1/5/83 |
| FDE-43 | Timberline Stables Control Sample (1 day) | 113 | Yes | Yes | Yes | 0.83 | 42 | Not Quenched | 12/17-12/18/82 | 1/5/83 |
| FDE-19 | Timberline Stables Control Sample (7 days) | 200 | Yes | Yes | Yes | 0.89 | 29 | 12/22/82 | 12/27/82-1/4/83 | 1/[illegible]/83 |
| FDE-21 | Timberline Stables Control Sample (7 days) | 203 | Yes | Yes | Yes | 0.83 | 82 | Not Quenched | 12/27/82-1/3/83 | 1/[illegible]/83 |
| FDE-22 | Timberline Stables Control Sample (7 days) | 191 | Yes | Yes | Yes | 0.77 | 64 | 12/22/82 | 12/27/82-1/6/83 | 1/[illegible]/83 |
| FDE-2 | Timberline Stables Control Sample (14 days) | 181 | Yes | Yes | Yes | 0.78 | 42 | 12/30/82 | 1/3-1/7/83 | 1/10/83 |
| FDE-20 | Timberline Stables Control Sample (14 days) | 237 | Yes | Yes | Yes | 0.82 | 85 | Not Quenched | 1/3-1/4/83 | 1/13/83 |
| FDE-107 | Timberline Stables Control Sample (14 days) | 183 | Yes | Yes | Yes | 0.77 | 81 | 12/30/82 | 1/3-1/4/83 | 1/13/83 |
| FDE-126 | Timberline Stables Control Sample - Spiked Initially With $^{37}Cl_4$-TCDD | 259 | Yes | Yes | Yes | 0.80 | 79 | Not Quenched | 12/17-12/18/82 | 1/11/83 |
| FDE-127 | Timberline Stables Control Sample - Spiked Initially With $^{37}Cl_4$-TCDD | 277 | Yes | Yes | Yes | 0.82 | 27 | Not Quenched | 12/16/82-1/4/83 | 1/13/83 |
| FDE-126B | Timberline Stables Control Sample - Spiked Initially With $^{37}Cl_4$-TCDD | 136 | Yes | Yes | Yes | 0.82 | 32 | 12/30/82 | 1/3-1/7/83 | 1/10/83 |
| FDE-128 | Timberline Stables Control Sample - Spiked Initially With $^{37}Cl_4$-TCDD | 238 | Yes | Yes | Yes | 0.80 | 65 | Not Quenched | 12/17-12/18/82 | 1/13/83 |
| FDE-69 | Denny Farm Control Sample (1 day) | 332 | Yes | Yes | Yes | 0.81 | 86 | Not Quenched | 12/17-12/18/82 | 1/5/83 |
| FDE-70 | Denny Farm Control Sample (1 day) | 287 (372) | Yes | Yes | Yes | 0.77 | 74 | 12/16/82 | 12/17-12/18/82 | 12/22/82 |
| FDE-71 | Denny Farm Control Sample (1 day) | 311 (316) | Yes | Yes | Yes | 0.80 | 25 | 12/16/82 | 12/17-12/18/82 | 1/5/83 (1/5/83) |
| FDE-72 | Denny Farm Control Sample (7 days) | 336 | Yes | Yes | Yes | 0.78 | 94 | Not Quenched | 12/27/82-1/6/83 | 1/7/83 |
| FDE-73 | Denny Farm Control Sample (7 days) | 203 (217) | Yes | Yes | Yes | 0.78 | 85 | 12/22/82 | 12/27/82-1/6/83 | 1/12/83 (1/10/83) |
| FDE-74 | Denny Farm Control Sample (7 days) | 200 (281) | Yes | Yes | Yes | 0.78 | 114 | 12/22/82 | 12/27/82-1/3/83 | 1/12/83 (1/10/83) |

TABLE 4 - Continued

RESULTS OF HRGC-LRMS ANALYSES OF EXTRACTS OF EPA/CINN. (IERL) SAMPLES UNDER VIAR & COMPANY SAS NO. 362-HQ FOR 2,3,7,8-TETRACHLORODIBENZO-p-DIOXIN (TCDD)

| USU Sample No. | Sample Identification | Concentration of 2,3,7,8-TCDD Found (nanograms TCDD/grams of sample)[a.,b.] | Observable Signal Response | | | Ratio of Intensities m/z 320 / m/z 322 | % Recovery of $^{37}Cl_4$-2,3,7 TCDD Internal Standard | Date Sample Quenched | Date Sample Extracted | Date Sample Analyzed on GC-MS |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | m/z 320 | m/z 322 | m/z 257 | | | | | |
| FDE-45 | Timberline Stables Sample Treated With K-120 (1 day) | 249 | Yes | Yes | Yes | 0.84 | 114 | 12/16/82 | 12/17-12/18/82 | 1/13/83 |
| FDE-3 | Timberline Stables Sample Treated With K-120 (1 day) | 225 | Yes | Yes | Yes | 0.78 | 81 | 12/16/82 | 12/17-12/18/82 | 1/11/83 |
| FDE-4 | Timberline Stables Sample Treated With K-120 (7 days) | 110 (85.4) | Yes | Yes | Yes | 0.81 | 60 | 12/22/82 | 12/27/82-1/4/83 | 1/5/83 (1/10/83) |
| FDE-5 | Timberline Stables Sample Treated With K-120 (7 days) | 166 (155) | Yes | Yes | Yes | 0.75 | 11 | 12/22/82 | 12/27/82-1/6/83 | 1/7/83 (1/10/83) |
| FDE-6 | Timberline Stables Sample Treated With K-120 (7 days) | 171 | Yes | Yes | Yes | 0.80 | 25 | 12/22/82 | 12/27/82-1/5/83 | 1/10/83 |
| FDE-7 | Timberline Stables Sample Treated With K-120 (14 days) | 145 | Yes | Yes | Yes | 0.82 | 13 | 12/30/82 | 1/3-1/7/83 | 1/10/83 |
| FDE-8 | Timberline Stables Sample Treated With K-120 (14 days) | 222 | Yes | Yes | Yes | 0.78 | 90 | 12/30/82 | 1/3-1/4/83 | 1/14/83 |
| FDE-9 | Timberline Stables Sample Treated With K-120 (14 days) | 236 | Yes | Yes | Yes | 0.86 | 90 | 12/30/82 | 1/3-1/4/83 | 1/16/83 |
| FDE-43A | Denny Farm Sample Treated With K-400 (14 days) | 298 | Yes | Yes | Yes | 0.80 | 86 | 12/30/82 | 1/3-1/7/83 | 1/11/83 |
| FDE-51 | Denny Farm Sample Treated With K-120 (1 day) | 271 | Yes | Yes | Yes | 0.82 | 99 | 12/16/82 | 12/17-12/18/82 | 1/4/83 |
| FDE-52 | Denny Farm Sample Treated With K-120 (1 day) | 331 | Yes | Yes | Yes | 0.79 | 100 | 12/16/82 | 12/17-12/18/82 | 1/4/83 |
| FDE-53 | Denny Farm Sample Treated With K-120 (1 day) | 279 | Yes | Yes | Yes | 0.78 | 100 | 12/16/82 | 12/17-12/18/82 | 1/4/83 |
| FDE-54 | Denny Farm Sample Treated With K-120 (7 days) | 86.7 | Yes | Yes | Yes | 0.70 | 33 | 12/22/82 | 12/17-1/4/83 | 1/5/83 |
| FDE-55 | Denny Farm Sample Treated With K-120 (7 days) | 191 | Yes | Yes | Yes | 0.78 | 96 | 12/22/82 | 12/27-82-1/3/83 | 1/7/83 |
| FDE-56 | Denny Farm Sample Treated With K-120 (7 days) | 205 | Yes | Yes | Yes | 0.78 | 84 | 12/22/82 | 12/27/82-1/6/83 | 1/10/83 |

TABLE 4 - Continued

RESULTS OF HRGC-LRMS ANALYSES OF EXTRACTS OF EPA/CINN. (IERL) SAMPLES UNDER VIAR & COMPANY SAS NO. 362-HQ FOR 2,3,7,8- TETRACHLORODIBENZO-p-DIOXIN (TCDD)

| USU Sample No. | Sample Identification | Concentration of 2,3,7,8-TCDD Found (nanograms TCDD/grams of sample)[a.,b.] | Observable Signal Response m/z 320 | m/z 322 | m/z 257 | Ratio of Intensities m/z 320 / m/z 322 | Minimum Detectable Quantity of 2,3,7,8-TCDD in Total Sample | % Recovery of $^{37}Cl_4$-2,3,7,8-TCDD Internal Standard | Date Sample Quenched | Date Sample Extracted | Date Sample Analyzed on GC-MS |
|---|---|---|---|---|---|---|---|---|---|---|---|
| FDE-57 | Denny Farm Sample Treated With K-120 (14 days) | 349 (366) | Yes | Yes | Yes | 0.78 | -- | 80 | 12/30/82 | 1/3-1/7/83 | 1/12/82(1/10/83) |
| FDE-56 | Denny Farm Sample Treated With K-120 (14 days) | 325 | Yes | Yes | Yes | 0.80 | -- | 109 | 12/30/82 | 1/3-1/4/83 | 1/14/83 |
| FDE-59 | Denny Farm Sample Treated With K-120 (14 days) | 262 | Yes | Yes | Yes | 0.81 | -- | 91 | 12/30/82 | 1/3-1/4/83 | 1/14/83 |
| FDE-108 | Acetone Blank Plus K-400 (2 days) | N.D. | No | No | No | -- | 14ng. | 27 | 12/17/82 | 12/17-12/18/82 | 1/13/83 |
| FDE-109 | Acetone Solution of 2,3,7,8-TCDD Containing 510ng. TCDD Treated With K-120 (2 days) | 452 | Yes | Yes | Yes | 0.82 | -- | 79 | 12/17/82 | 12/17-12/18/82 | 1/13/83 |
| FDE-110 | Acetone Solution of 2,3,7,8-TCDD Containing 510ng. TCDD Treated With K-400 (2 days) | 518 | Yes | Yes | Yes | 0.79 | -- | 39 | 12/17/82 | 12/17-12/18/82 | 1/4/83 |
| FDE-112 | K-400 Reagent Blank | N.D. | No | No | No | -- | 13ng. | 32 | 12/17/82 | 12/17/82-1/6/83 | 1/11/83 |
| FDE-112B | K-400 Reagent After Standing 4 days | N.D. | No | No | No | -- | 2ng | 89 | 12/20/82 | 12/20/82 | 1/11/83 |
| FDE-114 | Toluene Blank | N.D. | No | No | No | -- | 13ng. | 39 | 12/17/82 | 12/17/82-1/5/83 | 1/11/83 |
| FDE-115 | K-120 Reagent Blank | N.D. | No | No | No | -- | 16ng. | 9 | 12/17/82 | 12/17/82-1/6/83 | 1/11/83 |
| FDE-116 | Toluene Blank Plus K-120 | N.D. | No | No | No | -- | 3ng. | 73 | 12/17/82 | 12/17-12/18/82 | 1/13/83 |
| FDE-117 | Toluene Solution of 2,3,7,8-TCDD Containing 510ng. TCDD Treated With K-120 (2 days) | N.D. | No | No | No | -- | 4ng. | 61 | 12/17/82 | 12/17-12/18/82 | 12/22/82 |
| FDE-118 | Toluene Solution of 2,3,7,8-TCDD Containing 510ng. TCDD Treated With K-120 (4 days) | N.D. | No | No | No | -- | 5ng. | 51 | 12/20/82 | 12/20/82 | 1/4/83 |
| FDE-119 | Toluene Solution of 2,3,7,8-TCDD Containing 510ng. TCDD Treated With K-400 (4 days) | Indeterminate[c.] | -- | -- | -- | -- | -- | -- | 12/20/82 | 12/20/82 | 1/4/83 |

TABLE 4 - Continued

BRENM LABORATORY, WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435

RESULTS OF HRGC-LRMS ANALYSES OF EXTRACTS OF EPA/CINN. (IERL) SAMPLES UNDER VIAR & COMPANY SAS NO. 362-HQ FOR 2,3,7,8-TETRACHLORODIBENZO-p-DIOXIN (TCDO)

| WSU Sample No. | Sample Identification | Concentration of 2,3,7,8-TCDD Found (nanograms TCDD/grams of sample)a.,b. | Observable Signal Response m/z 320 | m/z 322 | m/z 257 | Ratio of Intensities m/z 320 / m/z 322 | % Recovery of $^{37}Cl_4$-2,3,7 TCDD Internal Standard | Date Sample Quenched | Date Sample Extracted | Date Sample Analyzed on GC-MS |
|---|---|---|---|---|---|---|---|---|---|---|
| DE-75 | Denny Farm Control Sample (14 days) | 278 | Yes | Yes | Yes | 0.80 | 65 | Not Quenched | 1/3-1/4/83 | 1/14/83 |
| DE-76 | Denny Farm Control Sample (14 days) | 423 | Yes | Yes | Yes | 0.79 | 89 | 12/30/82 | 1/3-1/4/83 | 1/14/83 |
| DE-77 | Denny Farm Control Sample (14 days) | 317 | Yes | Yes | Yes | 0.81 | 101 | 12/30/82 | 1/3-1/4/83 | 1/14/83 |
| DE-82 | Denny Farm Control Sample - Spiked Initially With $^{37}Cl_4$-TCDD | 178 | Yes | Yes | Yes | 0.81 | 78 | Not Quenched | 12/17-12/18/82 | 1/13/83 |
| DE-84 | Denny Farm Control Sample - Spiked Initially With $^{37}Cl_4$-TCDD | 358 | Yes | Yes | Yes | 0.85 | 22 | Not Quenched | 12/16/82-1/4/83 | 1/13/83 |
| DE-25 | Timberline Stables Sample Treated With K-400 (1 day) | 253 | Yes | Yes | Yes | 0.76 | 71 | 12/16/82 | 12/17-12/18/82 | 1/11/83 |
| DE-26 | Timberline Stables Sample Treated With K-400 (1 day) | 261 | Yes | Yes | Yes | 0.77 | 98 | 12/16/82 | 12/17-12/18/82 | 1/4/83 |
| DE-27 | Timberline Stables Sample Treated With K-400 (1 day) | 322 (211)(229) | Yes | Yes | Yes | 0.79 | 100 | 12/16/82 | 12/17-12/18/82 | 1/4/83 (1/12/83) (1/14/83) |
| DE-28 | Timberline Stables Sample Treated With K-400 (7 days) | 113 | Yes | Yes | Yes | 0.83 | 42 | 12/22/82 | 12/27/82-1/4/83 | 1/5/83 |
| DE-29 | Timberline Stables Sample Treated With K-400 (7 days) | 151 (179) | Yes | Yes | Yes | 0.80 | 79 | 12/22/82 | 12/27/82-1/6/83 | 1/7/83 (1/12/83) |
| DE-30 | Timberline Stables Sample Treated With K-400 (7 days) | 189 | Yes | Yes | Yes | 0.78 | 57 | 12/22/82 | 12/27/82-1/6/83 | 1/10/83 |
| DE-31 | Timberline Stables Sample Treated With K-400 (14 days) | 235 | Yes | Yes | Yes | 0.80 | 65 | 12/30/82 | 1/3-1/7/83 | 1/10/83 |
| DE-32 | Timberline Stables Sample Treated With K-400 (14 days) | 191 | Yes | Yes | Yes | 0.82 | 63 | 12/30/82 | 1/3-1/4/83 | 1/14/83 |
| DE-33 | Timberline Stables Sample Treated With K-400 (14 days) | 234 | Yes | Yes | Yes | 0.82 | 61 | 12/30/82 | 1/3-1/4/83 | 1/14/83 |
| DE-1 | Timberline Stables Sample Treated With K-120 (1 day) | 217 | Yes | Yes | Yes | 0.80 | 78 | 12/16/82 | 12/17-12/18/82 | 1/4/83 |



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TABLE 4 - Continued

RESULTS OF HRGC-LRMS ANALYSES OF EXTRACTS OF EPA/CINN. (IERL) SAMPLES UNDER VIAR & COMPANY SAS NO. 362-HQ FOR 2,3,7,8-TETRACHLORODIBENZO-p-DIOXIN (TCDD)

| USU Sample No. | Sample Identification | Concentration of 2,3,7,8-TCDD Found (nanograms TCDD/grams of sample)[a.,b.] | Observable Signal Response m/z 320 | m/z 322 | m/z 257 | Ratio of Intensities m/z 320 / m/z 322 | Minimum Detectable Quantity of 2,3,7,8-TCDD in Total Sample | % Recovery $^{37}Cl_4$-2,3,7,8-TCDD Internal Standard | Date Sample Quenched | Date Sample Extracted | Date Sample Analyzed on GC-MS |
|---|---|---|---|---|---|---|---|---|---|---|---|
| CE-120 | Toluene Solution of 2,3,7,8-TCDD Containing 510ng. TCDD Treated With K-400 (2 days) | Indeterminate[c.] | -- | -- | -- | -- | -- | -- | 12/17/82 | 12/17-12/18/82 | 12/22/82 |
| FDE-121 | Toluene Blank Plus K-400 | N.D. | No | No | No | -- | 11ng. | 34 | 12/17/82 | 12/17-12/18/82 | 1/11/83 |
| FDE-131 | Acetone Blank | N.D. | No | No | No | -- | 10ng. | 36 | 12/17/82 | 12/17/82-1/6/83 | 1/11/83 |

a. "N.D." indicates "Not Detected" at level in excess of minimum detectable quantity cited.

b. Numbers in parentheses indicate the results of replicate analyses of the same sample extract.

c. The toluene solution of TCDD was not miscible with the K-400 reagent and two distinct layers were apparent in the sample vessel. Therefore, a representative aliquot of the sample could not be obtained and the analysis did not yield useful results.

TABLE 5

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SUMMARY OF MEAN TCDD CONCENTRATIONS IN CONTROL AND KPEG-TREATED SOIL SAMPLES

VIAR & CO. SAS NO. 362-HQ

| SAMPLE IDENTIFICATION | SAMPLE TYPE | NUMBERS OF SAMPLES AVERAGED TO DERIVE MEAN | MEAN CONCENTRATION OF 2,3,7,8-TCDD (ng/g of sample) | MAXIMUM DEVIATION FROM THE MEAN |
|---|---|---|---|---|
| Timberline Stables | Control (Untreated) | 13(FDE-23,-24, -43,-19,-21, -22,-2,-20, -107,-125,-127, -128) | 225 | +23% -20% |
| | K-400 Treated-1 day | 5(FDE-25,-26, -27,-27,-27) | 255 | -- |
| | K-400 Treated-7 days | 4(FDE-31,-32, -32) | 158 | -- |
| | K-400 Treated-14 days | 3(FDE-31,-32, -33) | 220 | -- |
| | K-120 Treated-1 day | 3(FDE-1,-45, -3) | 230 | -- |
| | K-120 Treated-7 days | 5(FDE-4,-4,-5, -5,-6) | 137 | -- |
| | K-120 Treated-14 days | 3(FDE-7,-8,-9) | 201 | -- |
| Denny Farm Site | Control (Untreated) | 14(FDE-69,-70,-71) -72,-73,-74,-75, -76,-77,-92,-94) | 302 | +40% -34% |
| | K-400 Treated-14 days | 1 (FDE-63A) | 298[a] | -- |
| | K-120 Treated-1 day | 3(FDE-51,-52,-53) | 294 | -- |
| | K-120 Treated-7 days | 3(FDE-54,-55,-56) | 161 | -- |
| | K-120 Treated-14 days | 3(FDE-57,-58,-59) | 326 | -- |

a. Not a mean value.

# APPENDIX V

## PROTOCOL FOR SUPPLEMENTARY EXPERIMENTS TO DETERMINE FACTORS THAT CAUSED VARIABILITY IN TCDD SOIL TREATMENT DATA

# BREHM LABORATORY, WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435

## PROPOSED PROTOCOL FOR FURTHER EXPERIMENTS TO DEFINE FACTORS RESULTING IN THE VARIABILITY OF DATA ON TCDD CONCENTRATIONS IN SOILS AS DETERMINED BY GC-MS ANALYSES

Recent data on the concentration of 2,3,7,8-TCDD in soil samples which were obtained by the Brehm Laboratory in connection with experiments to evaluate the efficacy of certain chemical reagents for destruction of TCDD have exhibited considerable variability. In spite of the relatively large number of soil samples analyzed by the Brehm Laboratory (and a few other laboratories) in the course of numerous environmental assessments spanning several years, it has never been possible, because of the inevitable pressure from EPA and other clients to obtain data rapidly, to adequately define the primary factors which are responsible for the degree of variability in such analytical data. In addition, the precision and accuracy required for such determinations have not really been defined in most previous environmental assessments because the criteria for TCDD levels (in terms of "tolerable" levels) were not defined by EPA. Also, in the past such data has been obtained for a variety of different purposes, not all requiring highly precise data. In a study such as that currently in progress in our laboratory, in which TCDD concentrations in soils are being measured for the purpose of assessing the efficacy of chemical destruction techniques, the quality of the data becomes a very important factor, since it can critically affect the conclusions which are drawn in instances where it is necessary to observe relatively small changes in the TCDD concentration (as for example, in comparing treated and untreated soil samples).

In view of the above considerations, it is proposed to accomplish a series of experiments aimed at elucidating the factors which are responsible for the variability in the TCDD data obtained for soil samples. The data obtained thus far in the current study, which were presented in our report of Jan. 28, 1983 to Viar and EPA/IERL (Cinn.), suggest that one or more of several factors could be responsible for the observed variability and apparent trends in the TCDD data. Among these are:

1. The bulk soil samples from which portions were removed for use in the various soil treatment experiments may not have been adequately homogenized and the aliquots withdrawn may have been inconsistent in composition.

2. The extraction procedures utilized in the initial analyses may not have been sufficiently rigorous to remove all of the TCDD from the soil matrix, or may have extracted varying amounts of TCDD from the many aliquots analyzed (depending on the soil constituency and variations thereof). Evidence has been obtained that some types of particulates (especially fly ash and fine soils) are very difficult to extract reproducibly and completely, and may require rigorous extraction with particular solvents (aromatic solvents appear to be superior) in order to effectively remove tightly bound TCDD.

3. The addition of relatively large quantities of the reagents to the soil samples, which involves contact of the soil with both a strongly alkaline medium and a powerful solvent, may tend to free TCDD which was strongly bound to the soils, making simple extraction with organic solvents more effective. This process could conceivably be time dependent and could be increasingly effective as contact time of the reagent with the soil increases. If this were occurring, the quantity of TCDD which is extracted and observed would depend on the length of time between treatment and analysis.

4. Labelled $^{37}Cl$-TCDD added to all of the samples prior to analysis (but at different times following treatment and at various times before actual extraction) for use as an internal standard, may be increasingly bound up by the soils as the period for which it is allowed to remain in contact with the soil (prior to extraction) increases. This variability would be reflected in the data obtained for the native TCDD concentration, of course, since the latter is measured by reference to the $^{37}Cl$-TCDD internal standard.

5. The "quenching" procedures used in these experiments to destroy the remaining reagent in the samples prior to addition of the $^{37}Cl$-TCDD internal standard and analysis may not be completely effective, or the extent of its effectiveness may vary from sample to sample. This could result in continued TCDD degradation by the reagent following addition of the internal standard, thereby reducing its concentration in the sample, and distorting the analytical result for native TCDD. Also, if the quenching procedures were partially but not completely effective, the level of native TCDD in the sample at the time of measurement would be dependent upon the time between quenching and analysis, which obviously varies considerably in this study.

6. Treatment of the contaminated soils tested in this study with the reagents utilized may produce compounds which are not separated from TCDD by the cleanup procedures used and which exhibit gas chromatographic and/or mass spectrometric responses which interfere with those for TCDD. Alternatively, if the soils initially contain compounds which are TCDD "precursors", then perhaps treatment of the soils with the strong alkaline reagents used here actually generates TCDD.

7. Some of the observed variability in the TCDD data is undoubtedly due to variability in the analytical techniques themselves. The replicability of the various stages of the complex analytical sequence for determining TCDD in soils has not been adequately evaluated.

In an effort to determine the relative importance of the above factors as causes of the observed variability in the TCDD data for soils which are being chemically treated in the current tests, the following experiments are proposed.

A. Soil Homogeneity

A new bulk batch of TCDD contaminated soil will be prepared and attempts will be made to homogenize the sample more thoroughly than was accomplished for the Phase I tests. For these experiments, only the Denny Farm soil will be utilized, since it is higher in total organochlorine content, contains less water, and is generally finer in particle size than the other sample tested in Phase I (the Timberline Stables sample). These properties are all likely to maximize the probability of occurrence of problems such as those cited above, and so this soil should be a good choice for the experiments proposed here. In addition to screening and vigorously stirring the new bulk batch of soil prepared for these experiments (as was accomplished in the first phase studies) the soil will be mixed in a ball-mill (or equivalent) to more thoroughly homogenize it and produce more uniform particle size. Aliquots of this homogenized sample will be withdrawn and used for the experiments listed below.

B. Extraction Efficiency of Homogenized Denny Farm Soil

Three separate aliquots of the homogenized soil will be Soxhlet extracted with benzene for periods of 16, 24, and 32 hours respectively. Two other aliquots of the homogenized soil will be subjected to repetitive Soxhlet extraction with

benzene (using fresh solvent for each successive extraction) for three successive 16 hr. periods (or additional periods, if, at the end of three extractions, TCDD is still being removed from the soil). The results of these Soxhlet extractions will be compared with the results obtained by extracting two other aliquots of the homogenized soil by using the bottle extraction procedures applied in Phase I. These experiments should demonstrate whether or not more rigorous extraction of such soil samples is necessary.

C. Precision of GC-MS Analyses

Some of the sample extracts prepared in Step B. (by both the bottle and Soxhlet methods) will be repetitively analyzed on the GC-MS to provide a more statistically valid indication of the replicability of such measurements.

1) Successively withdraw 10 aliquots of each of two extracts (one prepared by Soxhlet and one by bottle extraction) and analyze on the GC-MS, on the same day as the extracts were processed.

2) Withdraw four aliquots of the same extract on each of three, five, seven and fourteen days after the extract was prepared and analyze on the GC-MS.

3) Successively withdraw aliquots of 1, 3, 5 and 10µl volume and analyze on the GC-MS.

D. Extraction of "Conditioned" Homogenized Soil

Separate batches of the homogenized soil will be "conditioned" by treating with selected chemicals which are either components of the KPEG reagents or are applied in the course of analysis, in an effort to determine if such chemicals affect the ability to extract TCDD and if this is a time-dependent phenomenon. These analyses will be accomplished taking into account the results obtained in Steps B and C.

1) A 50g. aliquot of the homogenized soil will be wetted with concentrated acid (HCl) and aliquots will be withdrawn at intervals of 1 hour, 1 day, 3 days, 7 days, and 14 days, and these will be Soxhlet extracted with benzene (for an appropriate period as determined in Step B, above) and analyzed for TCDD.

2) A 50g. aliquot of the homogenized soil will be wetted with concentrated base (KOH) and aliquots will be withdrawn at intervals of 1 hour, 1 day, 3 days, 7 days, and 14 days, and these will be Soxhlet extracted with benzene and analyzed for TCDD.

3) A 50g. aliquot of the homogenized soil will be wetted with polyethylene glycol (PEG) and aliquots will be withdrawn at intervals of 1 hour, 1 day, 3 days, 7 days, and 14 days, and these will be Soxhlet extracted with benzene and analyzed for TCDD.

E. Binding of TCDD to Soils - Effect of Time

Isotopically labelled ($^{37}Cl_4$-labelled) TCDD will be added to several aliquots of the homogenized soil (in separate beakers) in such a manner as to ensure uniform distribution on the soil. One of these samples will be Soxhlet extracted with benzene and analyzed for the $^{37}Cl$-labelled TCDD at intervals of 1 hour, 8 hours, 24 hours, 3 days, 1 week, and 2 weeks following application of the labelled TCDD.

F. Effects of Quenching the Destruction Reagents

These experiments will be conducted with a TCDD solution, since accomplishing them with spiked soil would not permit an independent evaluation of the effectiveness of the quenching procedure.

1) Determine the detailed time dependence for destruction of TCDD in a toluene solution of TCDD by K-120 by treating a solution of TCDD in toluene with K-120 and withdrawing successive aliquots of the treated solution at 1 hour intervals and analyzing these immediately for TCDD.

2) If the time for complete destruction of TCDD in the solution treated with K-120 is observed to be sufficiently long (several hours minimum), then prepare another TCDD solution in toluene, treat it with K-120 , allow the mixture to stand for a period sufficient to destroy about one-half of the TCDD, then add the quenching reagents used in previous phases of this study. Withdraw aliquots of the treated and quenched solution at intervals of 1 hour, 5 hours, 1 day, and 1 week following quenching and analyze for TCDD.

G. Search for Compounds in Treated Soils Which Exhibit GC and/or MS Responses Which May Interfere With TCDD Analyses

A more extensive effort will be made to identify products in the KPEG-treated soil samples which exhibit GC and/or MS responses which could interfere with TCDD analyses. In particular, evidence for possible adducts of TCDD will be sought. This will entail fractionation and more extensive mass spectrometric scanning analyses.